CHAPTER 3

ELECTRODEPOSITION OF SINGLE METALS

(Zinc and Tin)

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3.1 Electrodeposition of Single Metals (Zinc and Tin) :

Deposition of most metals from aqueous solutions especially at platinum cathode takes place with very little overvoltage and hence at essentially reversible potentials. 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 consequently 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 in. If the potential required for metal deposition is less than that for the hydrogen (or the reduction potential of the metal higher than that of hydrogen discharge at the cathode), the product of electrolysis at the cathod 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 (basic in particular) can be deposited, from aqueous solutions in preference to hydrogen, due to overvoltage of the latter.

It can readily be shown that in a neutral aqueous solution (pH = 7) the potential for the reversible evolution of hydrogen would be -

$$e_{H_2} = [illegible] - \frac{0.059}{1} \log \frac{1}{10^{-7}} = -0.41 \text{ volt.}$$

On the other hand, the deposition of most metals above hydrogen in E.M. Series would be impossible, were it not for overvoltage. For example, the deposition potentials for metals such as Zn (- 0.762 volt) or Sn (- 0.140 volt) suggest that hydrogen would preferentially be discharged first or alongwith the metals. But it has been shown that hydrogen overvoltage at copper or other cathode is much above the stated value. Consequently in order to discharge hydrogen from neutral solutions or even acidic ones containing the zinc or tin salts, a potential of about 1-0 volt would be necessary and as such the metals can easily be plated with relatively lower voltages without the gas evolution.

3.2 Electrodeposition of Zinc from Thiocyanate Bath :

Zinc can be deposited from both acid and alkaline baths. The acid baths consist of sulphate, chloride or fluoborate and the alkaline baths usually contain both cyanide(27) and zincate. phosphate baths are also alkaline. The alkaline baths have better throwing power and are therefore most commonly used to plate irregularly shaped articles. The acid baths are used to plate wire and sheet metal, where good throwing power is not required. Cyanide baths cannot be used to deposit zinc directly on malleable or cast iron unless special steps are taken in the preparation of the basic metals.

As indicated in introduction, hydrogen is much more easily discharged than zinc, as the potential of zinc is over 0.7 volt more negative than that of hydrogen. It appears therefore that it would be impossible to deposit zinc, at least with any good cathode efficiency, from acid solutions. The fact that it is possible to do so, depends upon the high over voltage of hydrogen on zinc. Actually as in Tainton process, zinc can be deposited with high cathode efficiences from strongly acid solutions, provided they are pure. The presence of very small amounts of certain metals such as cobalt and nickel, lowers the overvoltage of hydrogen on zinc and greatly decreases the cathode efficiency.

It is the objective of the present work, to obtain good quality deposit of zinc on copper from Thiocyanate bath (alkaline) which is very simple to prepare, with good throwing power and satisfactory CCE, so as to make the process commercially useful.

The following plating parameters were studied in order to obtain a good quality, lustrous and fine deposit.

1) Concentration of the electrolytes,
2) Current density,
3) Temperature,
4) Duration of electrolysis,
5) Electrode distance,
6) Addition agents.

3.2.1 Brief Review of the Earlier Work :

Thousands of Papers on electrodeposition of single metals are available. However the present review is confined to the deposition of Zinc and Tin.

3.2.2 Earlier Work on Electrodeposition of Zinc :

Cynaide zinc plating dates from World war-I, when the throwing power of the sulfate process was inadequate for plating steel shell castings. Commercial possibilities for the process were recognised and bath composition not too early postwar years by porotor and Wenlund (28) and Blum etal (29). Developmental highlights include the introduction by oplinger (30) of polysulfide for protection against metallic contamination. The historical aspects and performance of the more dilute baths are discussed by Bair (31) and Du Rose (32). A bath for electroplating of bright to semibright zinc of the acid chloride, acid sulphate, acid fluoborates, acid acetic acid sulphate, alkaline zincate or alkaline cynide type is described by Martin sylvia and co-workers (33). Similarly Huchette, Michel and others(34) gave the alkaline bath for electrodeposition of zinc, containing sodium hydroxide as main constituent and glyconic acid as complexing agent. Ammoniacal tetrafluoborate bath was given by Liushit(35) and others. Similar type of work has been done on different baths. Recently, quite promising work has been carried out on zinc deposition in relation to industrial aspects, addition agents structure etc. (36-54).

TABLE :- 1 : The effect of concentration of Zinc sulphate on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Potassium thiocyanate : 5 gms per 100 ml.
Current density : 1.6 amps per Sq.dm.
Duration of electrolysis : 20 minutes
Voltage : 1.9 to 2 volts.

Boric acid : 1 gm. per 100 ml.
Temperature : 30°C
Electrode distance : 4 cms.

Sr. No.	Concn.of Zinc sulphate (gms.per 100 ml)	Wt.of copper deposited in coulometer (in gms.)	Wt.of Zinc deposited (gms.)	CCE %	(Mean)	Nature of Deposit
1	5	0.065	0.024	35.91	(38)	Dull and adherent, black at the edges.
		0.068	0.028	40.00		
2	10 *	0.069	0.029	42.15	(41)	Uniform good, adherent and white bright.
		0.076	0.031	39.68		
3	15	-	-	-		Not so good but quite satisfactory.
4	20	0.069	0.036	51.01	(52)	Spongy, non adherent and black.
		0.067	0.037	53.21		
5	30	0.077	0.047	59.36	(61)	- do -
		0.075	0.046	62.46		
6	40	0.053	0.052	60.17	(65)	- do - unsatisfactory.
		0.069	0.062	69.66		

* Optimum condition.

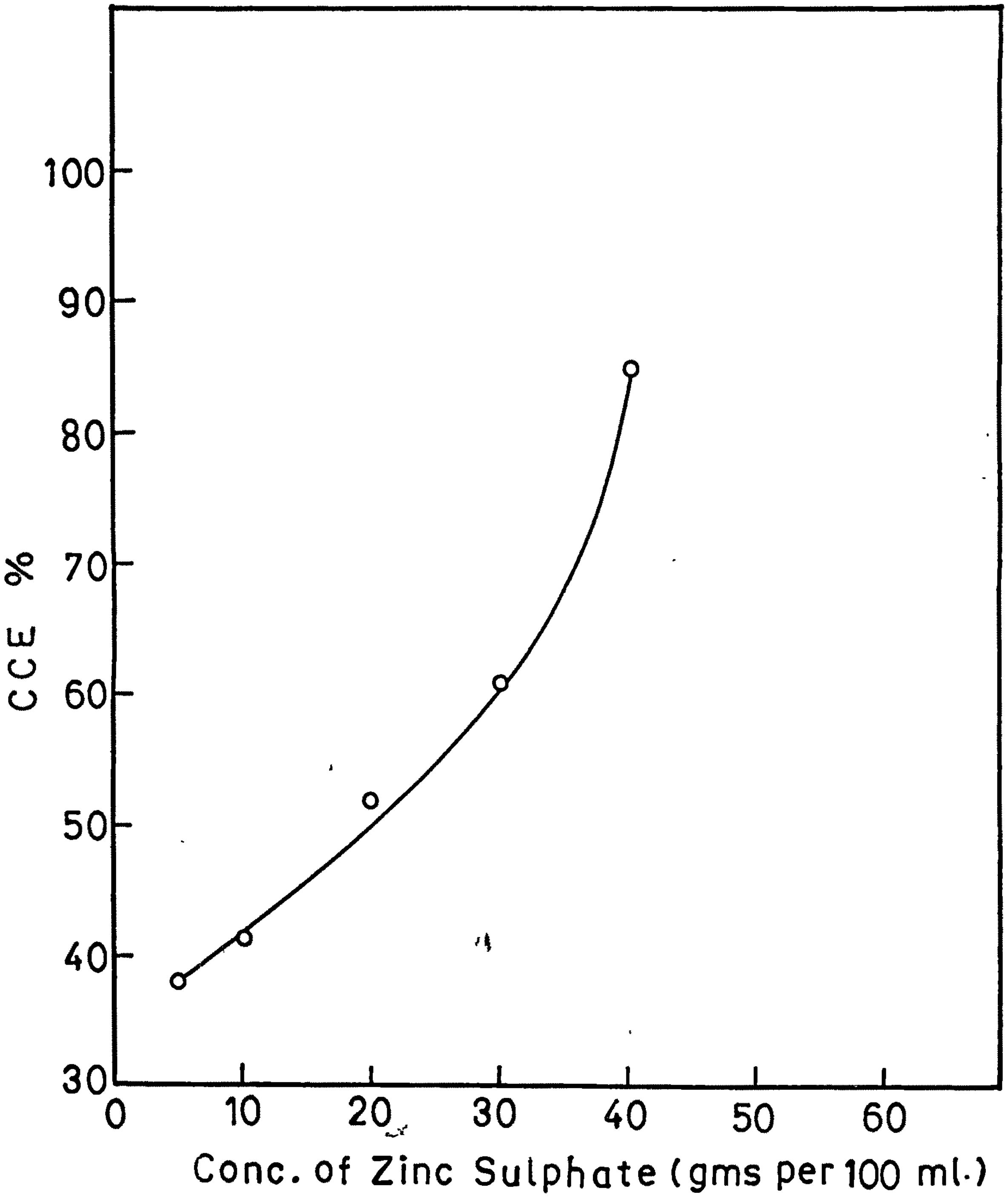

Fig. 1—Effect of Zinc Sulphate concentration on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO.2 :- The effect of concentration of potassium thiocyanate on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Current density : 1.5 amps per Sq.dm.
Duration of electrolysis : 30 minutes
Voltage : 1.5 to 1.9 Volts.

Boric acid : 1 gm. per 100 ml.
Temperature : 30 °C.
Electrode distance : 4 cms.

Sr. No.	Conc.of KCNS gms per 100 ml.	Wt.of copper deposited in coulometer gm.	Wt.of Zinc deposited gm.	Percentage CCE		Nature of deposit
1	1	-	-	-		Not satisfactory (dull deposit)
2	5	0.065	0.024	35.91	(38)	Uniform good adherent and bright
		0.062	0.023	40.00		
3	10 *	0.062	0.024	37.64	(37.0)	Improvement in quality.
		0.063	0.024	37.05		
4	15	0.063	0.025	38.2	(40.0)	Good deposit but blackening & treeing as time proceeds.
		0.059	0.025	41.00		
5	20	0.066	0.031	45.69	(45.0)	- do -
		0.071	0.033	45.20		
6	25	0.055	0.040	70.73	(69)	Adherent but non-uniform and spatchy.
		0.061	0.042	66.95		

* Optimum condition.

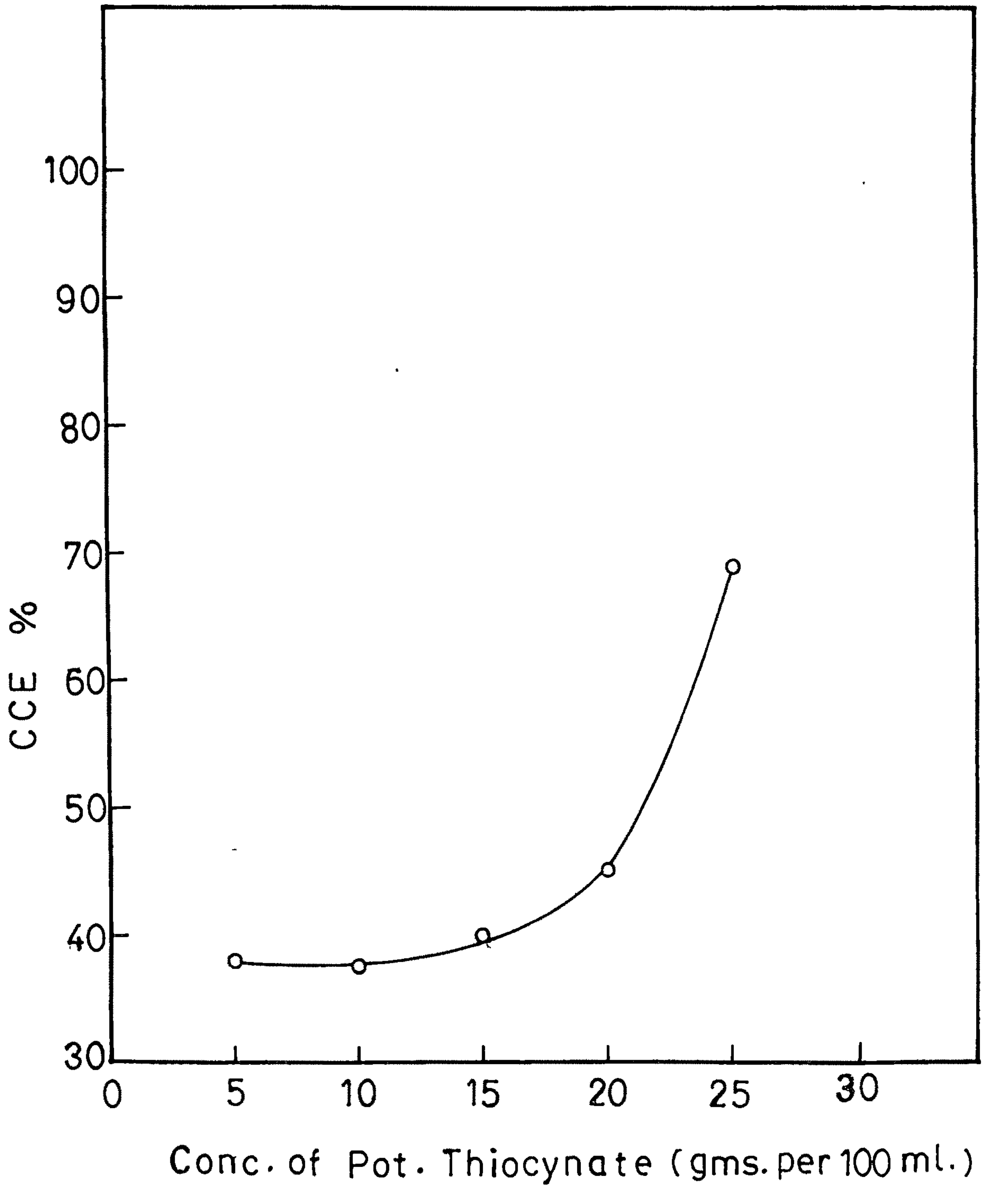

Fig. 2 — Effect of Potassium Thiocynate concentration on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO.3 :- The effect of concentration of Boric acid on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Zinc Sulphate : 10 gms. per 100 ml.
Current density : 1.6 amps per Sq.dm.
Duration of electrolysis : 20 minutes
Voltage : 1.9 to 2 Volts.

Potassium thiocyanate : 10 gms. per 100 ml.
Temperature : 30 °C.
Electrode distance : 4 cms.

Sr. No.	Conc.of Boric acid gms. per 100 ml.	Wt.of copper deposited in coulometer gms.	Wt.of Zinc. gms	Percentage CCE		Nature of deposit.
1	1	0.053	0.018	33.07	(34)	Uniform white bright, smooth and adherent.
		0.050	0.018	35.01		
2	2 *	0.054	0.043	77.45	(76)	Deposit improved in quality.
		0.053	0.041	75.26		
3	4	0.062	0.031	50.0	(50)	Uniform but slightly black.
		0.062	0.031	50.0		
4	6	0.060	0.023	37.27	(36)	Spongy, spatchy & unsatisfactory.
		0.063	0.029	35.66		
5	+ 8	0.051	0.021	33.17	(33)	- do -
		0.050	0.020	32.06		

* Optimum condition.

cf plate 1

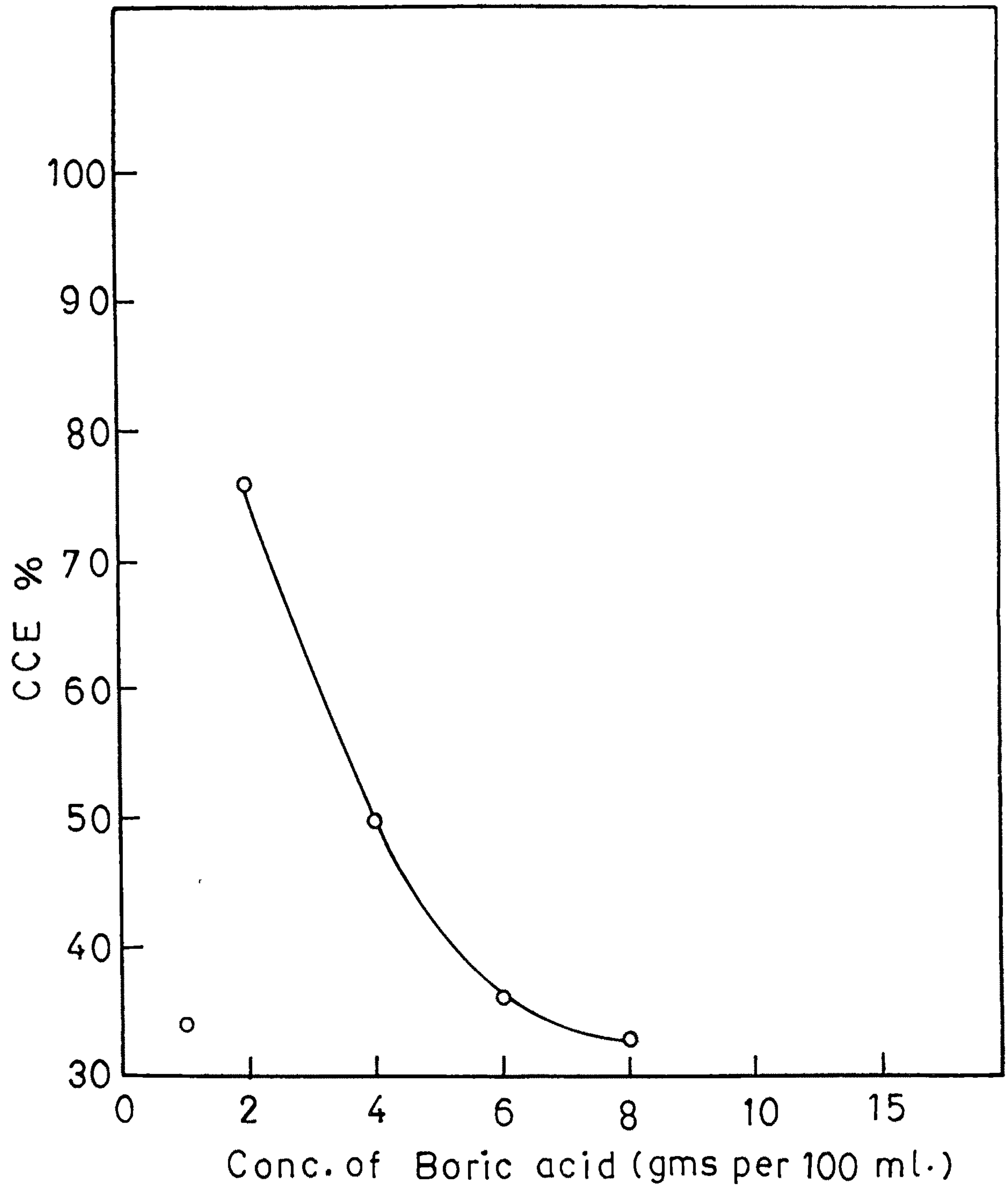

Fig.3—Effect of Boric acid concentration on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO.4 :- The effect of current density on the metal content and the percentage cathode current efficiency (CCE %) of the zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Boric acid : 2 gms. per 100 ml.
Duration of electrolysis : 20 minutes
Voltage : 1.7 to 2 volts.

Potassium thiocyanate : 10 gms. per 100 ml.
Temperature : 35°C
Electrode distance : 4 cms.

Sr. No.	Current density amp.per Sq. dm.	Wt.of copper deposit in coulometer gms.	Wt.of zinc deposited gms.	Percentage CCE		Nature of deposit.
1.	0.3	0.032	0.012	36.12	(39)	Spatchy with black spot, unsatifactory.
		0.030	0.013	41.76		
2	1.6	0.066	0.032	46.72	(47)	Uniform, bright and smooth deposit.
		0.064	0.033	49.69		
* 3	2.4	0.081	0.051	60.67	(60.9)	Bright, adherent, uniform, quite good.
		0.080	0.051	61.42		
+ 4	3.2	0.127	0.083	62.97	(64)	Smooth but slightly black.
		0.105	0.072	66.07		
5	4.0	0.133	0.113	82.76	(82)	Unsatisfactory. Spongy nonadherent, black with treeing at edges.
		0.134	0.114	81.97		

* Optimum condition.
+ cf Plate 2

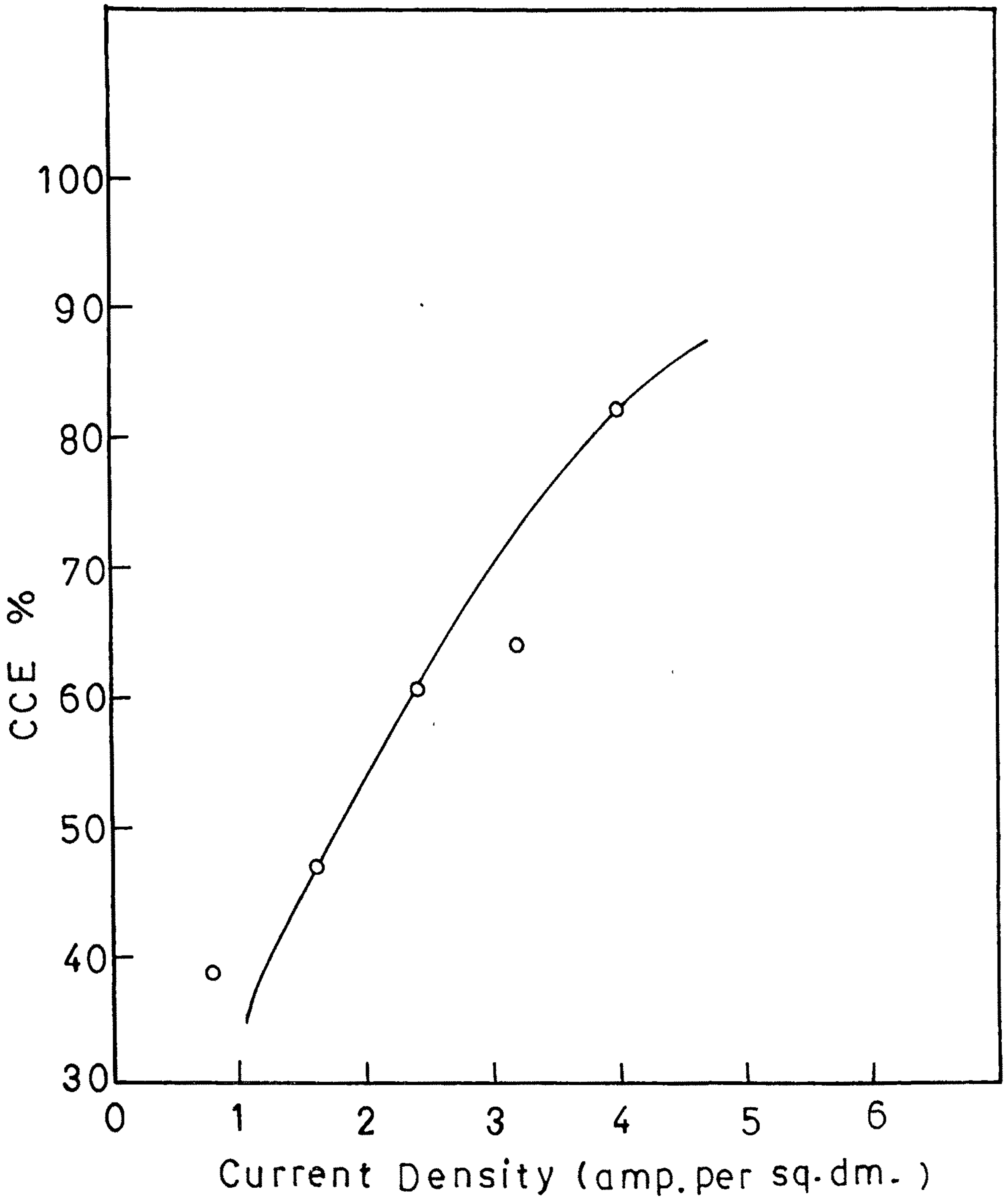

Fig. 4—Effect of current density on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO. 5 :- The effect of temperature on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Boric acid : 2 gms. per 100 ml.
Duration of electrolysis : 20 minutes.
Voltage : 2 volts.

Potassium thiocyanate : 10 gms. per 100 ml.
Current density : 2.4 amp per sq.dm.
Electrode distance : 4 cms.

Sr. No.	Temp. °C.	Wt.of copper deposited in coulometer gms.	Wt.of Zinc deposited gms.	Percentage CCE		Nature of deposit
1	10	0.054	0.041	73.03	(73)	Non uniform but adherent.
		0.055	0.041	72.49		
2	20	0.058	0.037	62.01	(63)	Good deposit but not uniform
		0.052	0.035	64.57		
3	* 30	0.068	0.032	47.15	(49)	Smooth bright and adherent.
		0.066	0.033	50.00		
4	40	0.064	0.026	39.13	(40)	Good deposit but slightly black. Slight evolution of gas.
		0.065	0.027	40.03		
5	+ 50	0.061	0.028	45.68	(44)	Dull and rough deposit. Not satisfactory.
		0.062	0.027	42.36		

* Optimum condition.
cf Plate 3.

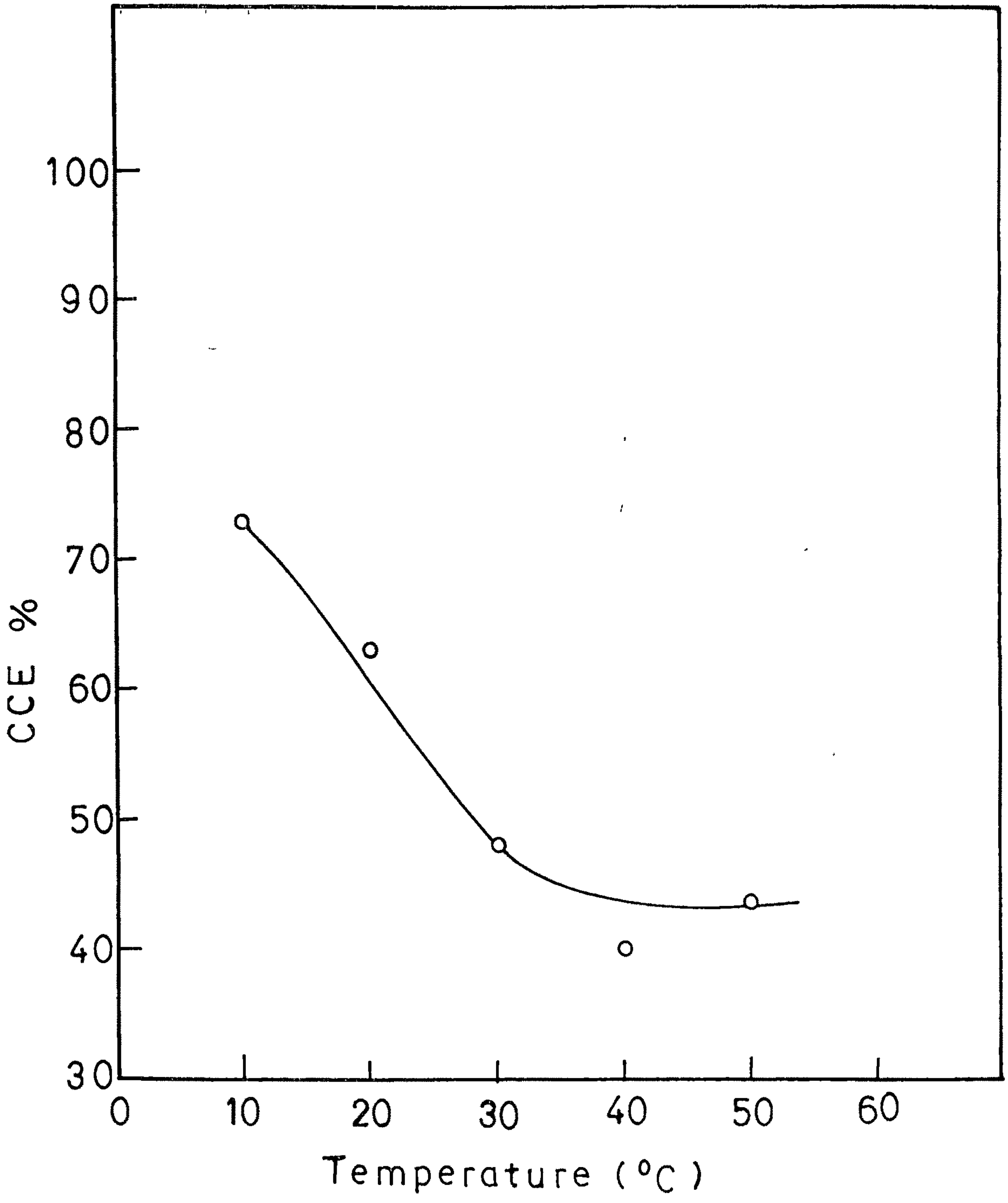

Fig. 5—Effect of temperature on cathode current efficiency (CCE %) of Zinc deposite.

TABLE NO.6 :- The effect of duration of electrolysis on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Boric acid : 2 gms. per 100 ml.
Temperature : 30 C.
Voltage : 2 volts.

Potassium Thiocyanate : 10 gms. per 100 ml.
Current density : 2.4 amp. per Sq.dm.
Electrode distance : 4 cms.

Sr. No.	Duration of electrolysis mins.	Wt.of copper deposited in coulometer gms.	Wt.of Zinc deposited gms.	Percentage CCE		Nature of deposit.
1	5	0.035	0.015	41.30	(40.0)	Smooth but slightly non-adherent.
		0.036	0.015	40.15		
2	10	0.083	0.060	69.66	(69)	Slight improvement.
		0.084	0.060	68.8		
* 3	15	0.097	0.087	86.42	(86)	Smooth and good. The colour of the bath solution is slightly pink.
		0.098	0.087	86.42		
4	20	0.130	0.113	83.76	(82)	Smooth and good deposit.
		0.134	0.114	81.97		
5	30	0.175	0.152	83.69	(84)	- do - blackish powder found to be adsorbed on the cathode.
		0.176	0.155	84.82		

* Optimum condition.

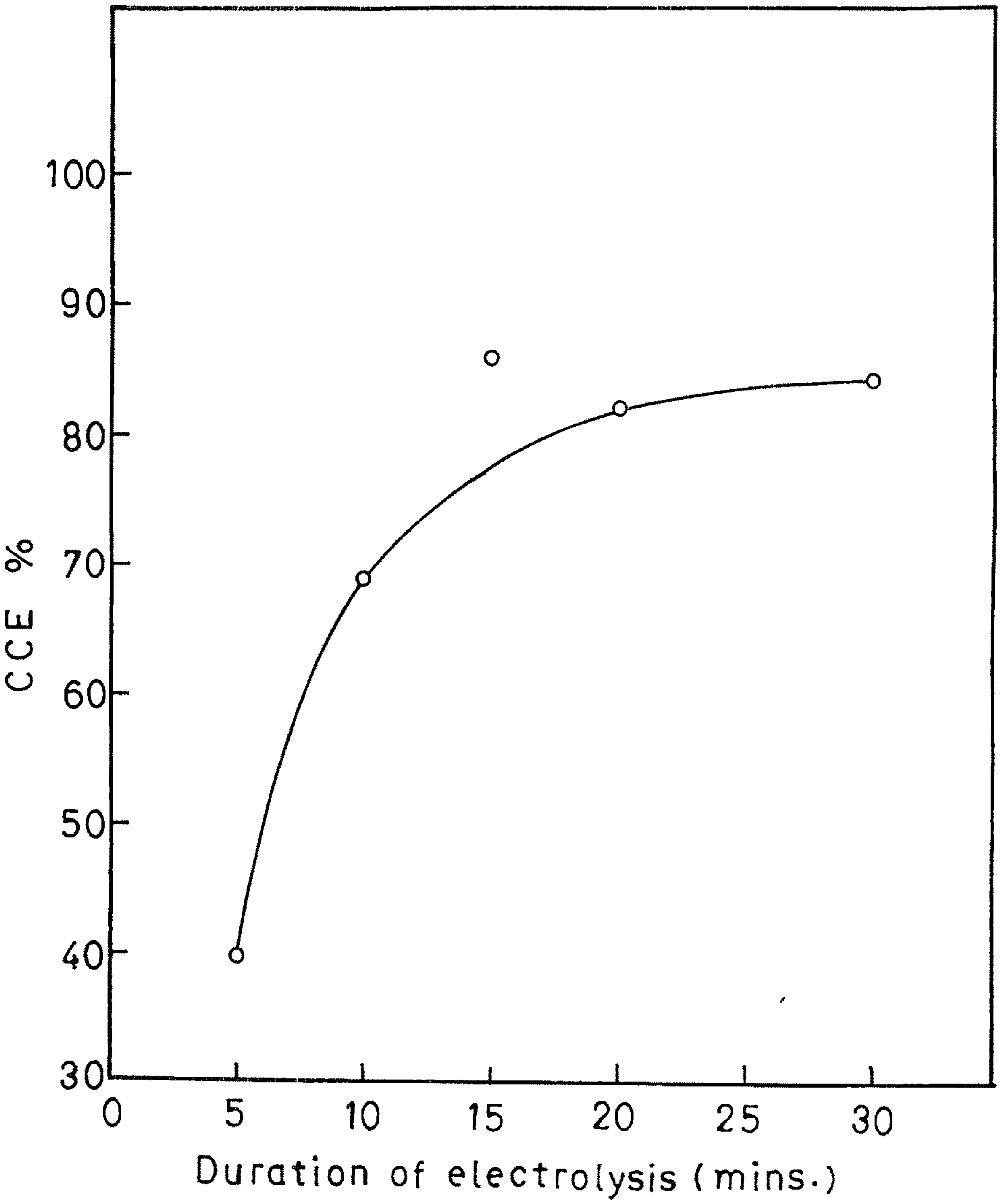

Fig. 6 — Effect of duration of electrolysis on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO.7 :- The effect of Electrode distance on the metal content and the percentage cathode current efficiency (C.C.E) of the Zinc Deposit.

Zinc sulphate : 10 gms. per 100 ml. Potassium thiocyanate : 10 gmsper 100 ml.
Boric acid : 2 gms. per 100 ml. Current density : 2.4 amp. per Sq.dm^2.
Temperature : 30°C. Voltage : 2 volts.

Sr. No.	Electrode distance cm.	Wt.of copper deposited in coulometer gms.	Wt.of Zinc deposited gms.	Percentage CCE		Nature of deposit.
1	1	0.082	0.053	62.28	(62.0)	Very smooth bright deposit.
		0.082	0.053	62.28		
2	+ 2	0.083	0.049	56.38	(57.0)	Not significant change
		0.083	0.050	58.04		
3	3	0.084	0.049	55.06	(56.0)	-do-
		0.082	0.048	56.41		
4	* 4	0.080	0.047	56.61	(56.0)	-do-
		0.082	0.047	55.41		
5	5	0.082	0.049	56.41	(56.0)	-do-
		0.080	0.047	55.41		

* Optimum condition.

\+ cf Plate 4.

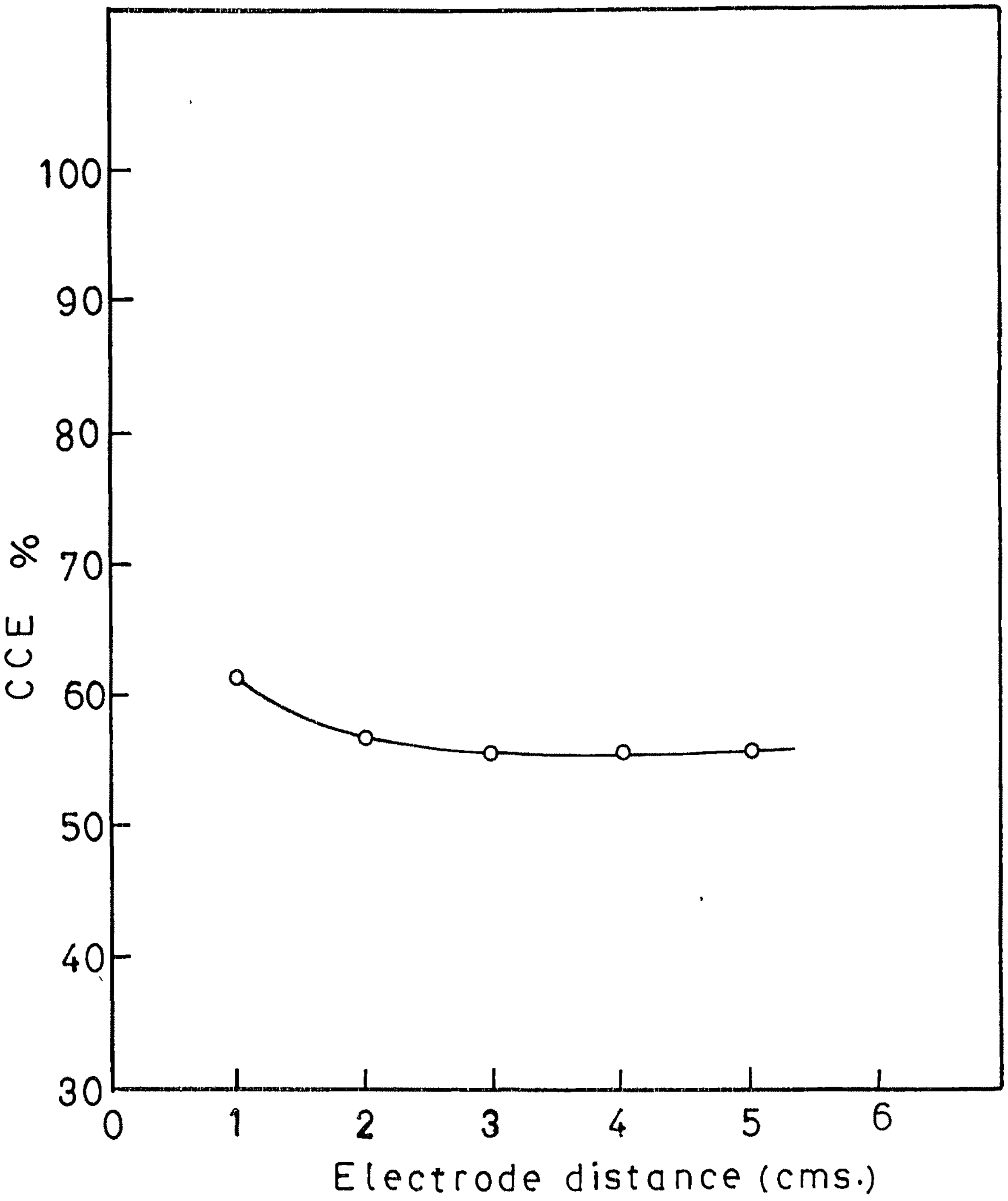

Fig. 7 — Effect of electrode distance on cathode current efficiency (CCE %) of Zinc deposit.

TABLE No.8 :- The effect of addition agents on the metal content and the percentage cathode current efficiency (CCE %) of the Zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Boric acid : 2 gms. per 100 ml.
Temperature : 30°C.
Voltage : 2 volts.

Potassium thiocyanate : 10 gms. per 100 ml.
Current density : 2.5 amp.per sq.dm.
Electrode distance : 4 cms.

Sr. No.	Addition agent	Amount per 100 ml. gms.	Wt.of copper deposited in coulometer gms.	Wt.of Zinc deposited gms.	Percentage CCE		Nature of deposit.
1	Agar	0.3	0.050	0.020	38.54	(38.0)	Smooth bright uniform.
			0.050	0.020	38.54		
2	Gelatine	0.3	0.050	0.021	40.47	(40.0)	Not satisfactory.
			0.051	0.021	39.67		
3	Gum	0.3	0.053	0.022	39.99	(40.0)	Smooth
			0.051	0.022	41.66		
4	+ Glucose	0.3	0.057	0.024	40.57	(41.0)	Smooth bright. Very lustrous
			0.057	0.025	42.65		
5	Formaldehyde	- 1 ml.	0.060	0.027	43.36	(42.0)	- do -
			0.061	0.027	42.65		

+ cf Plate 5

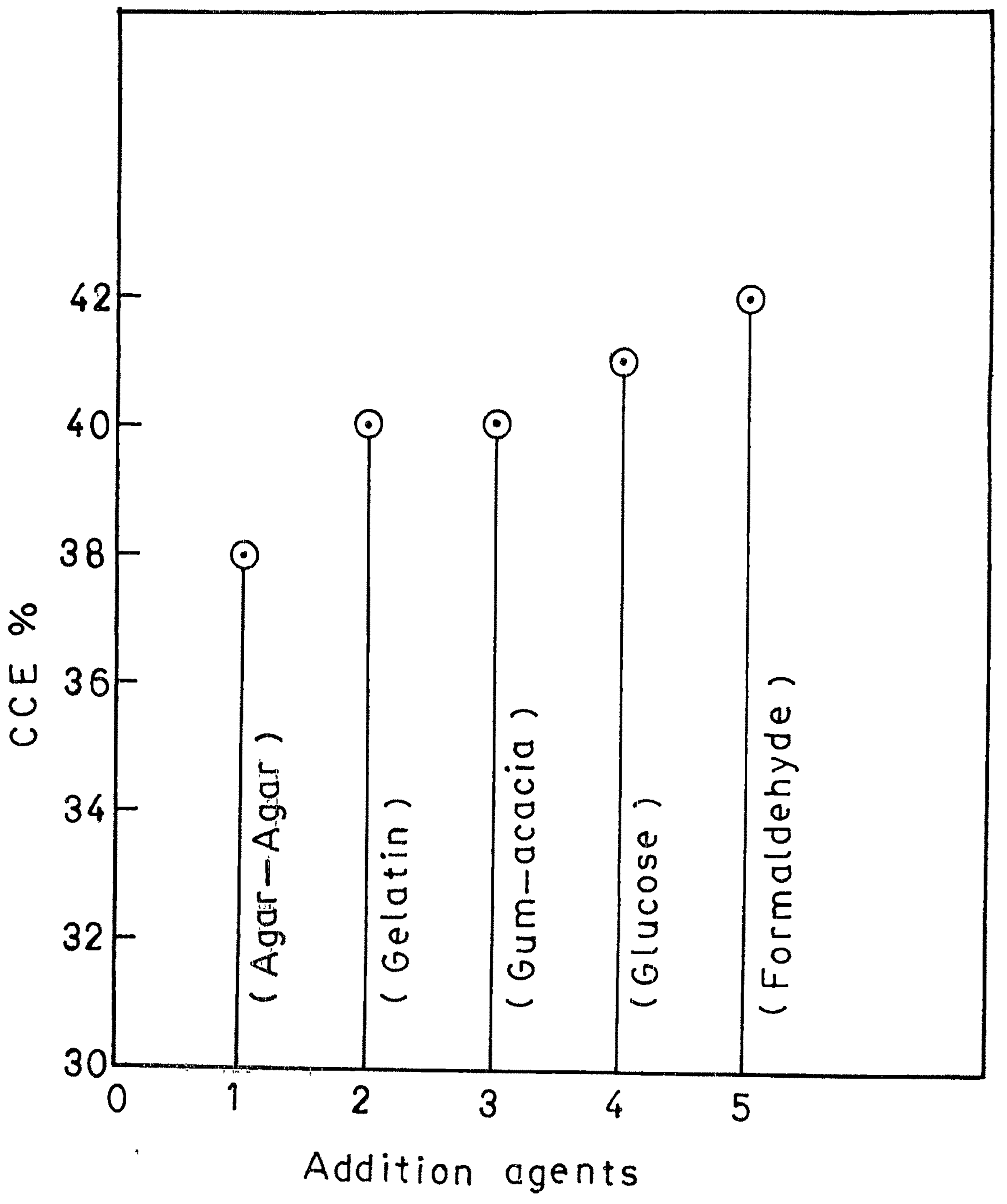

Fig. 8 — Effect of addition agents on cathode current efficiency (CCE %) of Zinc deposit .

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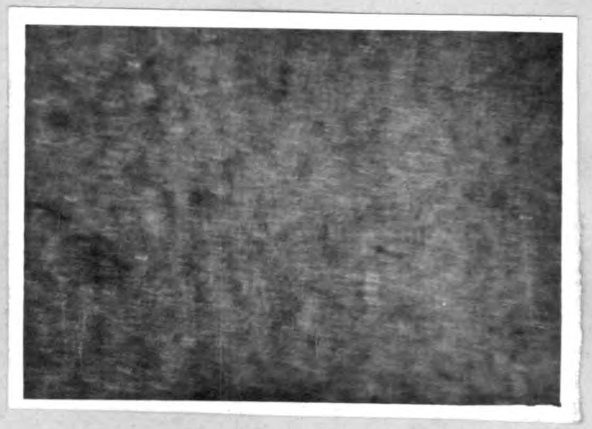
SUMMARY

Zinc System (Optimum Conditions)

Table 8B: The influence of the physico-chemical factors upon the nature and magnitude of the zinc deposit has been shown in the previous Table Nos. 1 to 8 and in Figs 1 to 8. The ranges over which the parameters were studied and the optimum conditions arrived at by experiments are summarised below:

Parameters studied and Range	Optimum condition
1) Composition of the bath.	-
a) Concn. of zinc sulphate 5-40 gms per 100 ml. of the solution.	10 gms. per 100 ml. of the solution.
b) Concn. of Potassium thiocynate 1-25 gms per 100 ml. of the solution.	10 gms. per 100 ml. of the solution.
c) Concn. of Boric acid 1-8 gms. per 100 ml of the solution.	2 gms. per 100 ml. of the solution.
2) Current density 0.8-4.0 amps. per sq. dm.	2.4 amps. per Sq. dm.
3) Temperature 10°-50°C	30°C.
4) Duration of electrolysis 5-30 minutes.	15 minutes.
5) Electrode distance 1-5 cms	4 cms.



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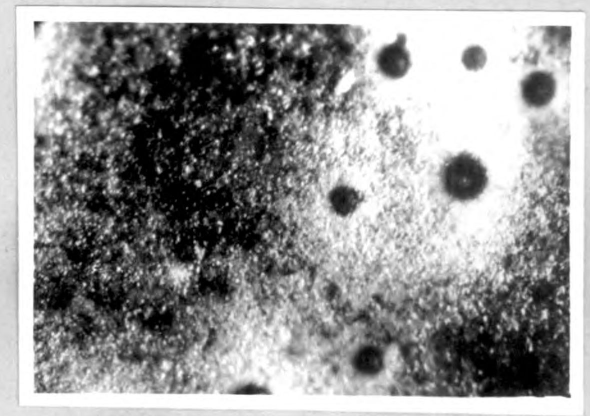

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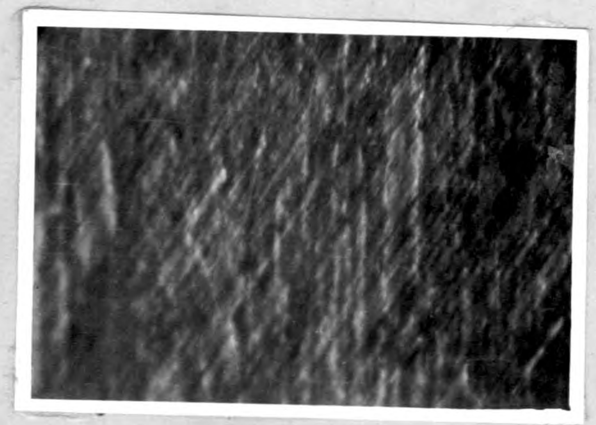

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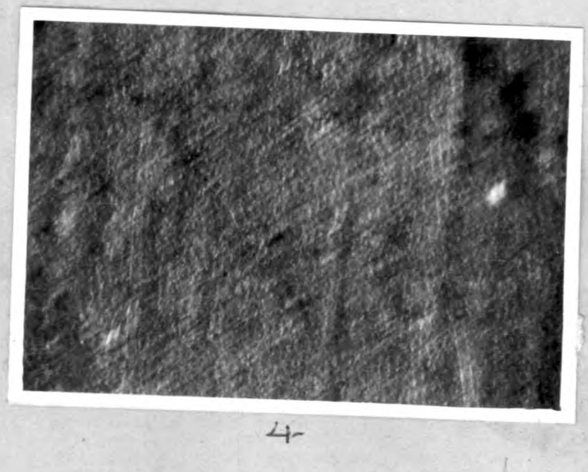

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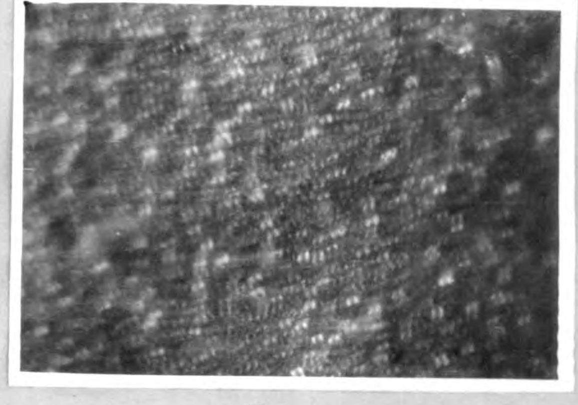

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c.f. plate 1-5 (Zinc)

3.3 Results and Discussion for Zinc : (Table 1-8, Figs 1-8)

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

ELECTROLYTE CONCENTRATION :

1) Effect of Zinc Sulphate Concentration : (Cf Table -1, Fig-1)

Effect of Zinc Sulphate concentration was studied between 5 gms. to 40 gms. per 100 ml. of the solution. Dull, spongy, non-adherent as well as smooth uniform and good deposits were obtained at different concentrations. At low concentration (5 gms. per 100 ml.) as well as at high concentration dull, spongy, and black deposits were obtained. This indicates that neither low or high concentration of zinc sulphate was beneficial for good quality deposit. However, it was observed that concentration of zinc increased in the deposit with increase in the concentration of zinc sulphate. At the same time CCE was also increased with increase in the concentration of zinc sulphate and reached maximum at high concentration (40 gms, per 100 ml.). The optimum condition for zinc sulphate concentration was 10 gms. per 100 ml. of zinc sulphate.

2) Effect of potassium thiocynate concentration (Cf table 2, Fig.2) :

Potassium thiocynate was introduced to the bath as a solvent. The amount of potassium thiocynate was varied from

1 gm to 25 gms. per 100 ml. For low concentration range the quality of deposit improved as there was increase in the concentration. However at high concentrations the blackening of the deposit occurs as time proceeds. Side by side treeing effect was also observed, particularly to the edges of the plate. The amount of zinc deposited remained mostly constant during the range. There was no marked effect as such on the CCE. The optimum condition was obtained at 10 gms. of potassium thiocynate per 100 ml.

3) <u>Effect of Boric acid concentration (Cf.Table-3, Fig.3):</u>

Boric acid has a marked effect on the nature of deposit and especially on CCE. With increase in the concentration of Boric acid, the CCE was found to increase, it reached maximum and then decreased with further increase in the concentration of Boric acid. At moderate concentration, the deposits were bright smooth and adherent. However at higher concentrations, the deposits were spongy and nonadherent. The optimum condition for Boric acid concentration was 2 gms. per 100 ml.

4) <u>Effect of Current Density (Cf. Table - 4, Fig - 4):</u>

Using a bath of optimum composition, current densities varying from 0.8 to 4.0 A/dm^2 were studied. In the lower region of current density (0.8 A/dm^2), the deposits were dull, cloudy and patchy but with an increase in current density upto 2.4 A/dm^2 . Zinc grained more shining and adherent deposits, were obtained. Above this current density, the deposits turned black and showed burning effect (4.0 A/dm^2). This is always the case observed at high C.D. due to rapid depletion of the metal ions from the neighbourhood of the cathode. However, it was observed that with increase in the current density, CCE also increases. The optimum condition for current density was 2.4 A/dm^2 , when the deposit obtained was bright and uniform.

5) Effect of Temperature : (Cf Table - 5, Fig. 5) :

An increase in temperature in general, decreases the polarisation of the more nobel metal relatively more than the polarisation of the less nobel metal and causes an increase in the crystal size. The temperature range studied was 10°- 50°C, under optimum conditions of bath composition, and C.D. At very low temperature the deposits obtained were not satisfactory. however by increasing the temperature, good deposits were obtained. The influence of temperature is caused by greater solubility and dissociation of the metal salt, which in turn, leads to a higher conductivity of the solution. A high temperature increases the mobility of the metal ions and decreases the viscosity of the solution. Another advantage of high temperature is that there is usually less absorption of hydrogen in the deposits and less stress and tendency towards cracking.

The deposits obtained at temperature greater than 30°C. were with black tinge. At very high temperature (50°C), dull and rough deposit was produced. Zinc content in the deposit and its CCE decreases proportionately with an increase in the temperature.

The optimum condition obtained for temperature was 30°C.

6) Effect of duration of electrolysis (Cf Table 6 Fig - 6):

Under optimum conditions, the period of electrolysis varied from 5-30 minutes. Zinc metal content in the deposit was increased from about 40 % to 84 % with increase of time from 5 minutes to 30 minutes. CCE also changed from 40 to 84%. Thus with increase in duration CCE increases upto 86 % and then nearly remains constant. At optimum condition i.e. 15 minutes, the deposit obtained was smooth and good. At longer times, the blackish powder found to be adsorbed on cathode. The optimum conditions was that of 15 minutes.

7) Effect of Variation of electrode, distance (Cf Table-7, Fig - 7) :

The electrode distance between anode and cathode was changed between 1.0 - 5 cms. It was noticed that the character of the deposit as well as the composition and CCE, was not affected. This is because whenever the anode and cathode are separated by such distances that the equipotential surfaces approach planes (i.e. straight lines in the sectional drawings) then any further increase in the spacing, has no appreciable effect upon the current distribution.

B) Effect of Addition agents (Cf. Table - 8, Fig - 8):

It is well known that even small quantities of certain substances added to a depositing solution markedly influence the structure of the resulting deposit. These are called addition agents which can be well defined as substances which, while not necessary ingredients, are intentionally added to deposition baths in traces to produce a beneficial changes in the character of the deposit.

There is no fundamental principle underlying the use of these materials. But addition agents as a rule, exert the most favourable effect upon the deposit. Almost all addition agents are colloids. It had been thought that by adsorption in the deposit they may cause the metal to collect as very small crystals and cause a smooth deposit. The crystal growth at those points will be faster.

The addition agents listed in Table - 7, were introduced singly to the bath under optimum conditions and the effect was studied. Agar Agar, Gum, Glucose, Formaldehyde improved the character of deposit by promoting brightness. However, the deposits were not satisfactory in presence of gelatin. The stability was not affected by the use of the addition agents listed. The deposit, composition and CCE remained more or less the same.

3.6 Electrodeposition of Tin from Acid Chloride Bath :

Methods for the electrodeposition of tin, from either acid sulfate or alkaline solutions, have been known for more than 100 years. Morewood and Rogers (55) were granted a British patent on tin plating as early as 1843. Methods of tin deposition are summarized in two articles (56). In the acid baths the tin is present as stannous salt (ex. $SnCl_2$) while in alkaline baths it is present as stannic (ex Na_2SnO_3). The most important difference in these baths is the greater throwing power of the alkaline stannate baths, however the acid bath has the advantage that the valence of tin in it is II, compared with IV in the stannate bath, hence twice as much tin is deposited, at 100 percent efficiency, per ampere-hour in the acid as in the alkaline bath. The cathode efficiency is usually 95 % in acid bath and may be only 75 % in alkaline bath. The conductivity of the acid bath is higher than that of alkaline.

The substitution of tin plating for hot dipping of sheet steel for use in canning industry (57) came about through the wartime. Tin is not normally protective to steel, but in the particular conditions obtaining inside the sanitary can (sanitary meaning containing foods, or beverages) the usual potentials of tin and iron are revered and tin becomes protective. Tin plating of steel for use in the 'tin can' is the largest single use of electroplating in terms of tonnage of products.

Tin plating electrolytes in acid baths, usually the sulphate and the chloride, fluoride electrolytes, commerically known as the "Ferrostan" and "Halogen" processes, respectively, have achieved worldwise acceptance by the electrotinplate producers (58). Although tin may be deposited from many of the soluble acid tin salts, only three types of tin solutions stannous sulphate, stannous fluoborate and halogen formulations are in common use.

In 1942 the Grasselli-du pont organization, in response to request from weirton steel company, evaluated the stability of various tin plating solutions leading to the development of "Halogen Tin" process. The process was based on a solution of stannous chloride, plus alkali metal chlorides and fluorides with suitable addition agents, patents issued to Schweikher ( ), Hoffmann ( ) and Grey et al ( ) formed the original basis for the "Halogen Tin" process. A review by Du Rose ( ) of the early developments of the process indicates that the transition from pilot plant to full scale production at a speed of 300 m/min was achieved in one year. Much credit goes to Grasselli research team and the weirton steel company (60).

It is the objective of the present investigation to offer a simple acid bath (acid - chloride) in preference to the other acid or alkaline baths reported earlier (55-60), giving good quality deposit with a high CCE (over 90 %) even on copper, iron and other base metals. The bath is easy to handle, and gives good reproducibility of results.

3.4.1 Earlier work on Electrodeposition of Tin :

Number of methods for the electrodeposition of tin from different baths have been known for more than 100 years. Mathers and co-workers (61) tested many of these early baths and found non satisfactory. Forester (62) hinted at the reason. All were based on sodium stannite formed from a stannous salt in the presence of excess alkali.

Proctor (63) and Praine were apparenly to first to publish a plating bath based on sodium stannate. As far as acids baths for tin plating are concerned, number of investigations were involved in solving the problem with the additives which they found were necessary to give smooth and adherent deposit. (64).

Research on tin electredeposition continued at a rapid pace after 1960. Numerous articles and patents have appeared in the literature describing new addition agents, brighteners, crystal structure, effect of temperature, throwing power etc. (65 to 70).

TABLE NO. 9 :- The effect of concentration of the tin chloride on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Hydrochloric acid : 1.2 Tin mixture.
Current density : 0.4 amps per Sq.dm.
Duration of electrolysis : 30 minutes
Voltage : 1 Volt.

Sodium chloride : 2 gms per 100 ml.
Temperature : 27° C.
Electrode distance : 4 cms.

Obs. No.	Concn.of tin chloride per 100 ml. gms.	Wt.of copper deposited in coulometer gms	Wt.of tin deposited gms	CCE %	(Mean)	Nature of deposit
1	2	0.032	0.052	86.75	(86)	White, adherent with little trees formation.
		0.032	0.051	85.53		
2	3	0.029	0.048	87.60	(88)	Fine adherent with no tree formation.
		0.029	0.048	87.60		
3	* 4	0.029	0.050	91.50	(92)	-do- Slight improvement shining and satisfactory.
		0.029	0.050	91.50		
4	5	0.030	0.053	93.57	(93)	White, adherent.
		0.030	0.052	91.90		

* Optimum condition.

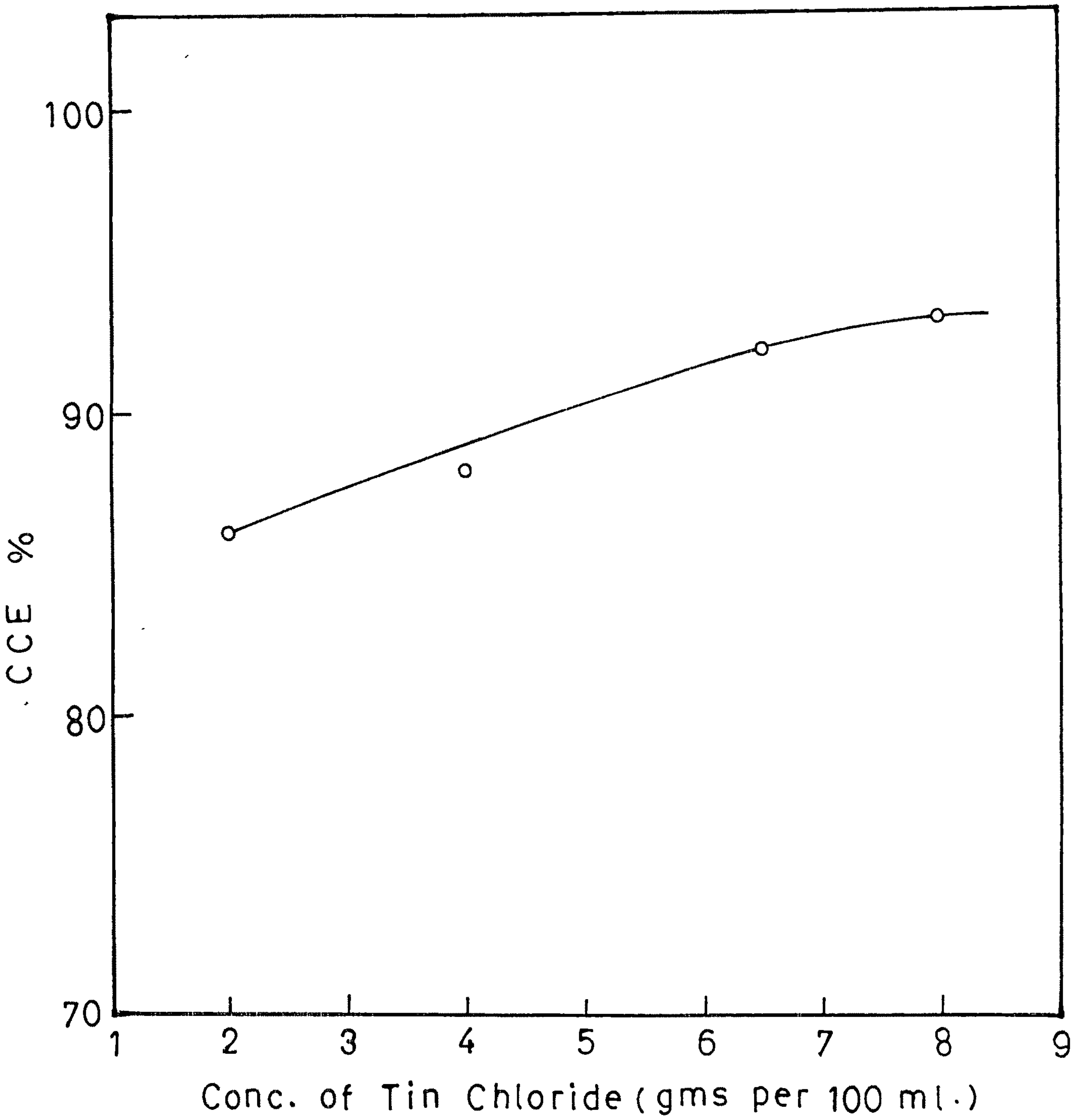


Fig. 9 – Effect of Tin Chloride concentration on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.10 :- The effect of concentration of hydrochloric acid on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride : 4 gms. per 100 ml.
Sodium chloride : 2 gms. per 100 ml.
Current density : 0.42amps per Sq.dm.
Temperature : 20°C.
Duration of electrolysis : 30 minutes.
Electrode distance : 4 Cms.
Voltage : 1 Volt.

Obs No.	Conc.of hydrochloric acid. Normality in mixture N.	Wt.of copper deposited in coulometer gms.	Wt.of tin deposited Gms.	CCE %	(Mean)	Nature of deposit.
1	0.4	0.032	0.061	100.1	(98)	Uniform,adherent and thick. The solution turns greenish yellow after some time.
		0.029	0.053	95.9		
2	0.6	0.029	0.050	94.75	(95)	- do -
		0.028	0.050	94.75		
3	* 0.8	0.029	0.049	89.67	(93)	Fine adherent, uniform, shining.
		0.029	0.050	94.78		
4	1.2	0.030	0.051	90.22	(92)	Fine,adherent little tree formation.
		0.030	0.053	93.75		
5	1.6	0.032	0.049	93.0	(93)	Adherent,evolution of gas at cathode.
		0.032	0.049	92.6		

* Optimum condition.

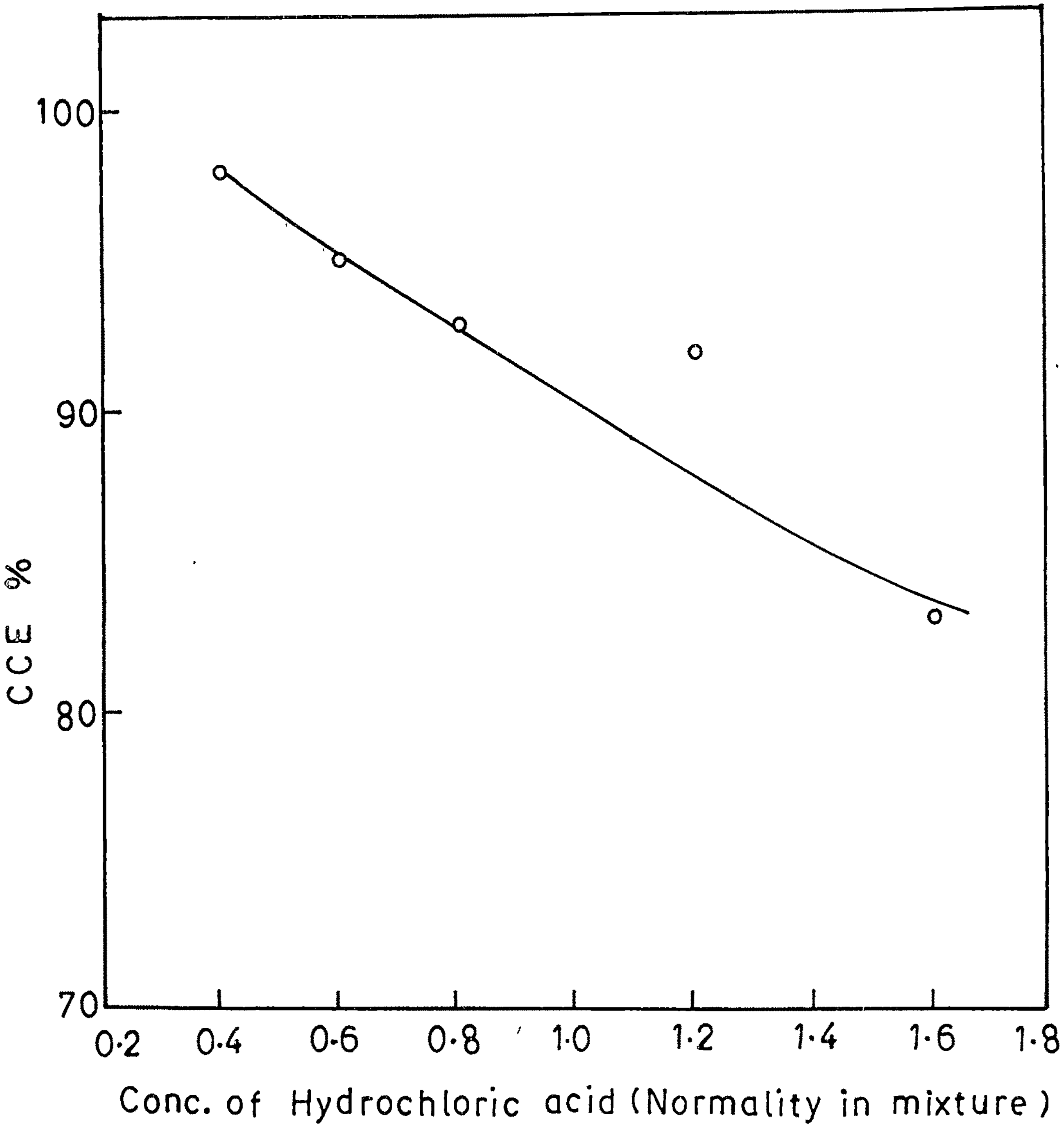


Fig. 10 —Effect of Hydrochloric acid concentration on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.11 :- The effect of concentration of sodium chloride on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride : 4 gms. per 100 ml.   Hydrochloric acid : 0.2 N in mixture.
Current density : 0.42amps per Sq.dm. Temperature : 20°C.
Duration of electrolysis : 30 minutes. Electrode distance : 4 Cms.
Voltage : 1 Volt.

Obs. No.	Concn.of sodium chloride per 100 ml. gms.	Wt.of copper deposited in coulometer gm.	Wt.of tin deposited gm.	CCE %	(Mean)	Nature of deposit.
1	2	0.027	0.049	96.31	(95)	Fine adherent and uniform
		0.033	0.059	94.00		
2	3	-	-	-		- do -
3	* 4	0.029	0.049	89.67	(91)	More silvery and lustrous than previous
		0.031	0.054	92.44		
4	5	0.030	0.051	90.22	(90)	-do- Slight tree formation tendency.
		0.031	0.052	89.88		
5	6	0.028	0.049	92.57	(89)	Evolution of gas. Not satisfactory.
		0.031	0.051	87.31		

* Optimum condition.

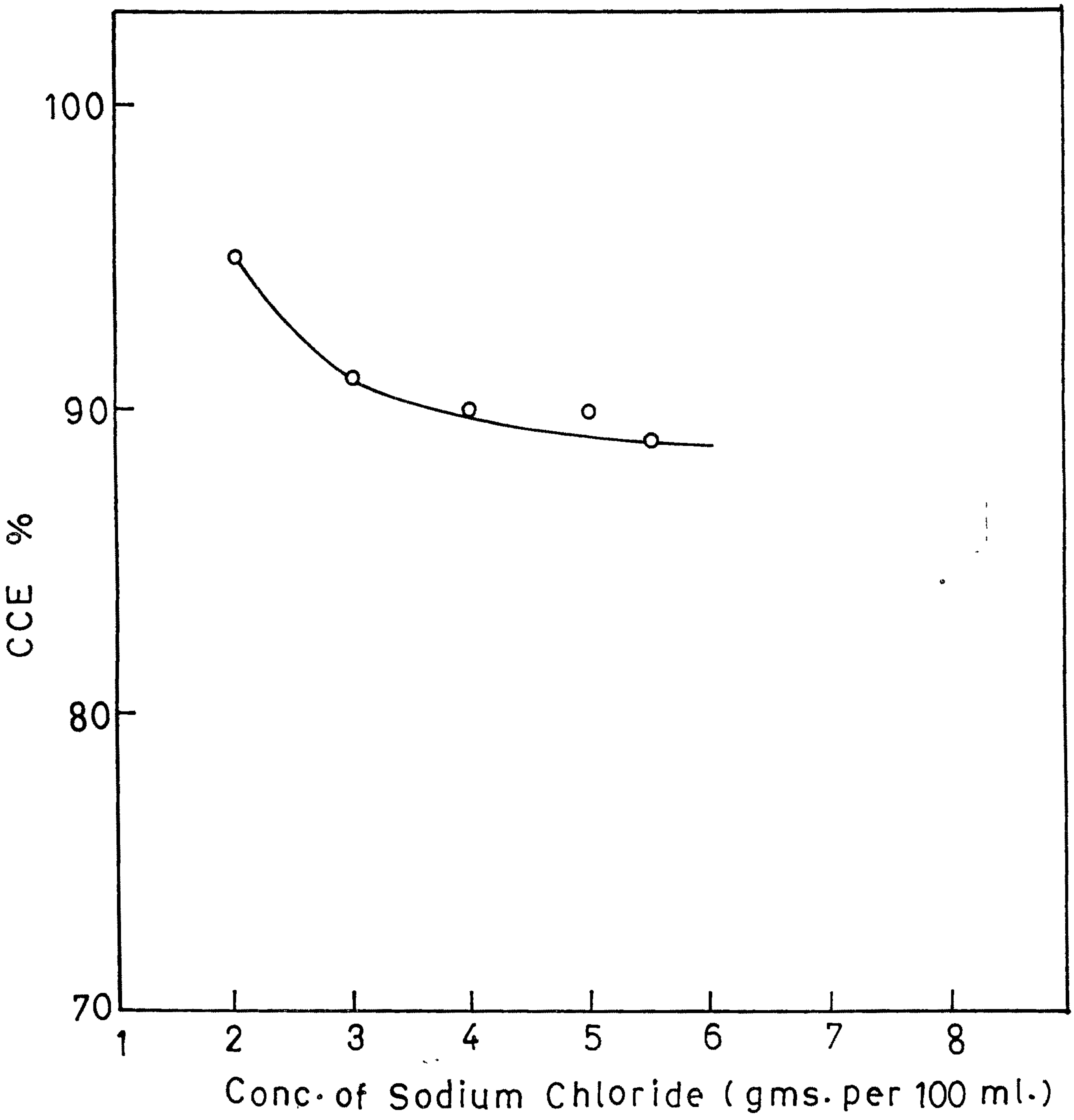


Fig. 11 — Effect of Sodium Chloride concentration on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.12 :- The effect of current density on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride : 4 gms per 100 ml.
Sodium chloride : 4 gms. per 100 ml.
Duration of electrolysis : 30 minutes.
Voltage : 1 to 3 Volts.
Hydrochloric acid : 0.8 N in mixture.
Temperature : 28°C.
Electrode distance : 4 Cms.

Obs. No.	Current density amps.per Sq. dm.	Wt.of Copper deposited in coulometer gms.	Wt.of tin deposited gms.	CCE %	(Mean)	Nature of deposit.
1	0.084	-	-	-		Non adherent unsatisfactory.
2	0.25	0.015	0.022	77.94	(78)	Adherent and dull.
		0.016	0.022	77.94		
3	* 0.42	0.026	0.044	89.32	(87)	Adherent,bright and fine.
		0.029	0.047	85.16		
4	0.63	0.049	0.082	90.66	(91)	-do- Tree formation tendency.
		0.049	0.082	90.66		
5	0.84	0.050	0.086	91.29	(91)	Tree formation tendency increases.
		0.050	0.086	91.29		
6	+ 1.04	-	-	-		Non adherent,Not satisfactory.

* Optimum condition.
\+ cf plate 6.

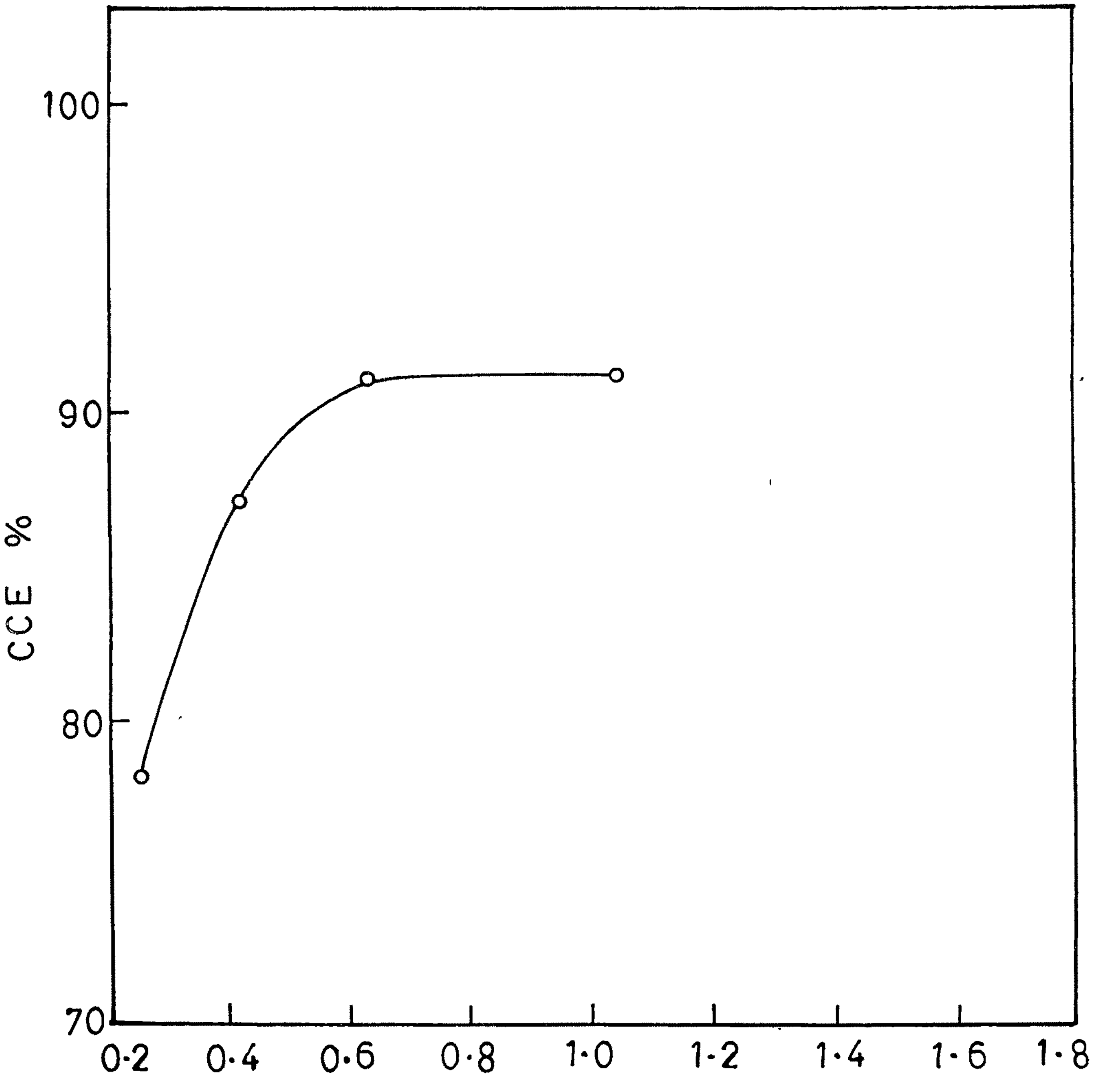


Fig.12 – Effect of current density on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.13 :- The effect of temperature on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride : 4 gms.per 100 ml.
Sodium chloride : 4 gms. per 100 ml.
Duration of electrolysis:30 minutes.
Voltage : 1 Volt.

Hydrochloric acid : 0.8 N in mixture
Current density : 0.42 amps.per Sq.dm.
Electrode distance : 4 cms.

Obs. No.	Temperature °C	Wt.of copper deposited in coulometer gms.	Wt.of tin deposited gms.	CCE %	(Mean)	Nature of deposit.
1	10	0.030	0.055	97.30	(97)	Non-adherent, white.
		0.030	0.055	97.30		
2	20	0.030	0.054	95.92	(96)	Adherent, bright.
		0.029	0.053	96.99		
3	* 30	0.029	0.048	87.84	(88)	Very fine, adherent, bright.
		0.030	0.050	88.45		
4	40	0.029	0.036	65.88	(67)	Adherent,nonuniform,bright.
		0.027	0.035	69.79		
5	+ 50	0.025	0.018	36.74	(36)	Dull,adherent,evolution of gas.
		0.027	0.018	35.93		

* Optimum condition. + cf Plate 7.

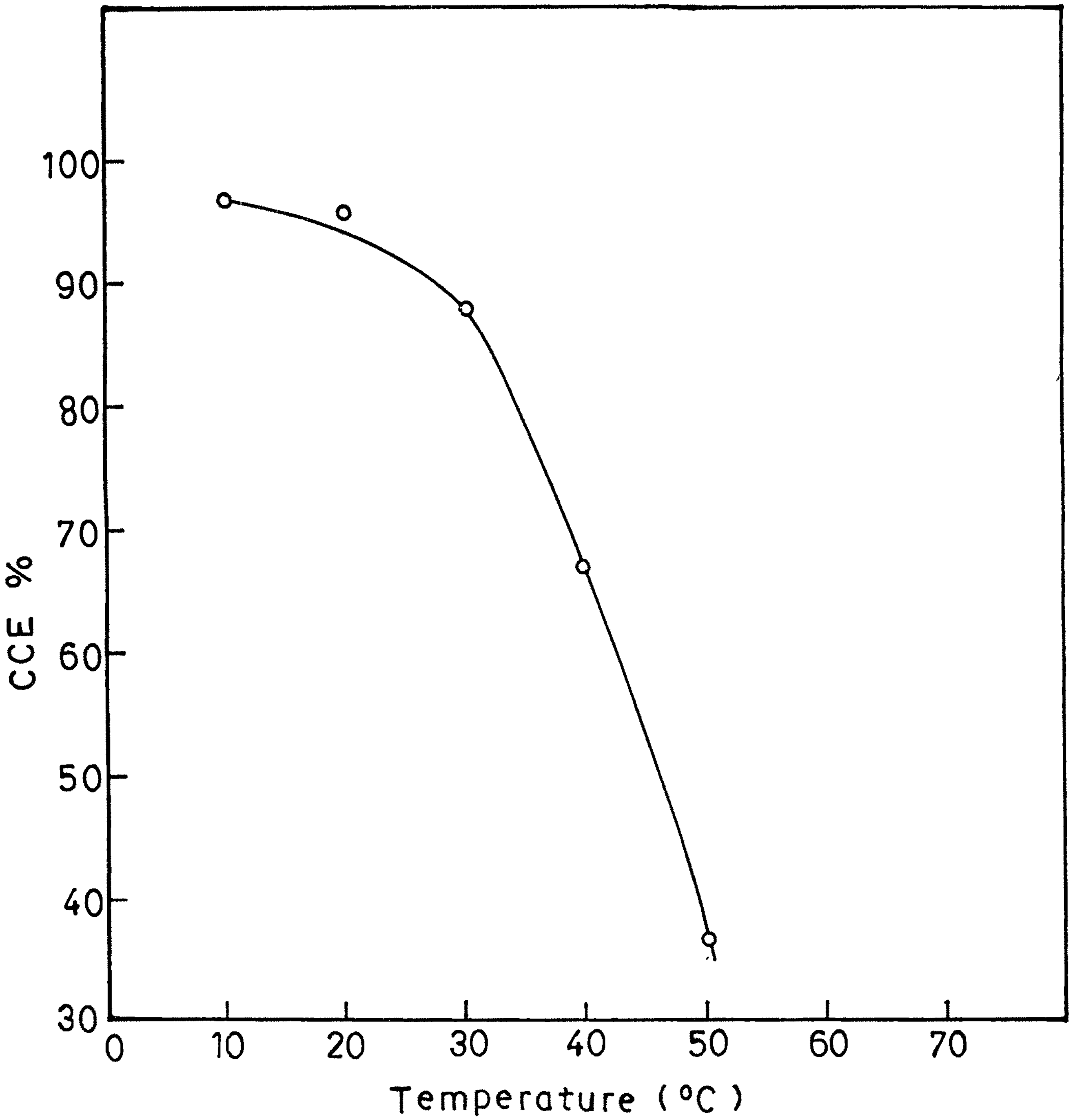


Fig. 13 – Effect of temperature on cathode current efficiency (CCE %) of Tin deposit .

TABLE NO.14:- The effect of duration of electrolysis on the metal content and the percentage cathode current efficiency (C.C.E %) of tin deposit.

Tin chloride : 4 gms. per 100 ml.
Sodium Chloride : 4 gms. per 100 ml.
Temperature : 30°C .
Voltage : 1 Volt.

Hydrochloric acid : 0.8 N. in mixture.
Current density : 0.42 amps.per Sq.dm.
Electrode distance : 4 cms.

Obs. No.	Duration of electrolysis minutes.	Wt.of Copper deposited in coulometer gm.	Wt.of tin deposited gms.	C.C.E %	(Mean)	Nature of deposit.
1	10	0.009	0.017	100	(100)	Nonuniform but adherent.
		0.009	0.017	100		
2	+ 20	0.016	0.030	99.51	(99)	Uniform, smooth bright, adherent.
		0.015	0.028	99.06		
3	* 30	0.029	0.049	99.67	(99)	Very fine, adherent, bright.
		0.030	0.050	98.45		
4	40	0.040	0.064	84.91	(85)	-do - Little tree formation tendency.
		0.040	0.065	86.24		
5	50	-	-	-		-do- tree formation tendency increases.

* Optimum condition. + cf. Plate 8.

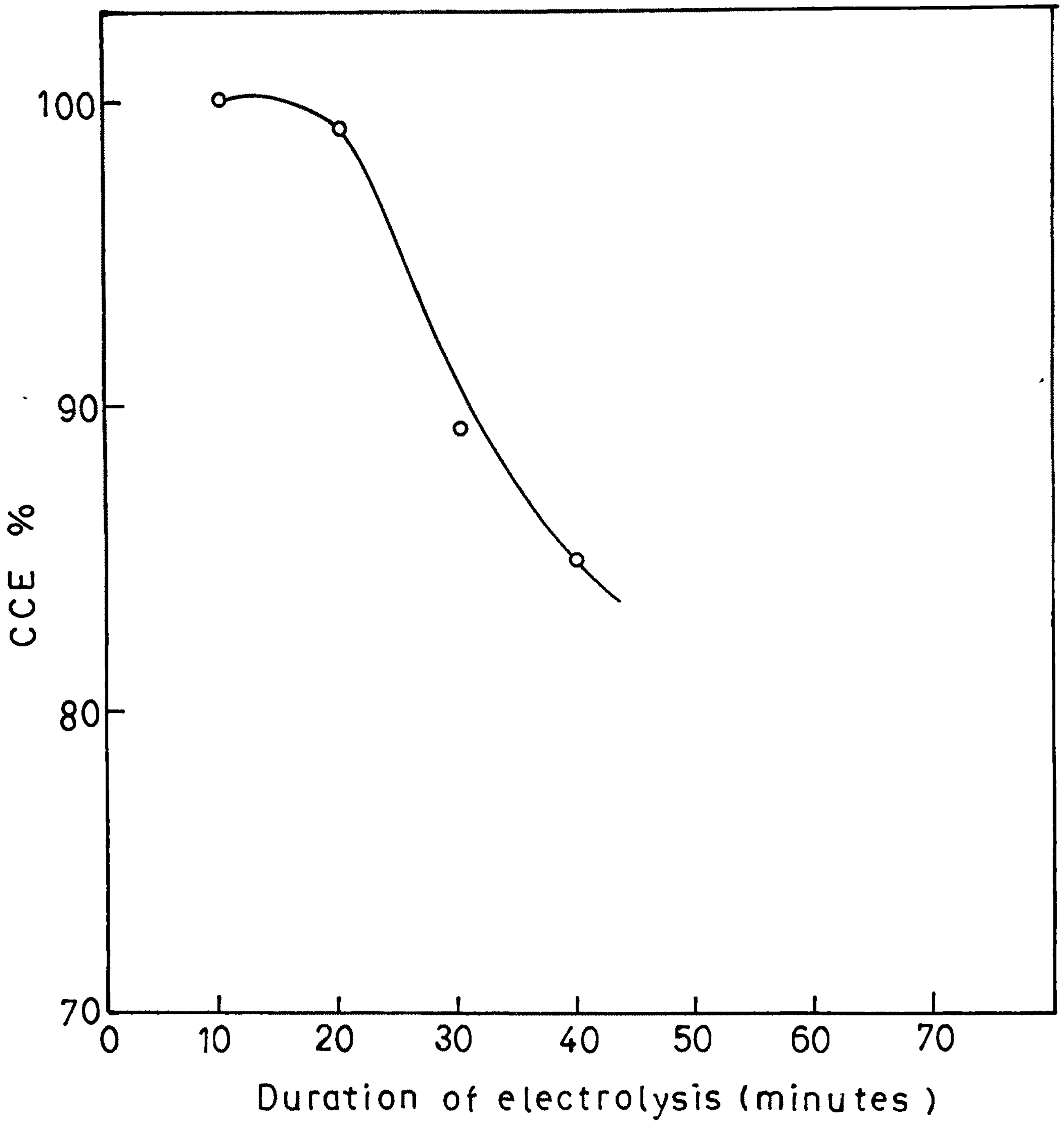


Fig. 14 —Effect of duration of electrolysis on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.15 :- The effect of electrode distance on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride: 4 gms. per 100 ml.
Sodium chloride : 4 gms per 100 ml.
Temperature : 30°C
Voltage : 1 Volt.

Hydrochloric acid: 0.8 N in mixture.
Current density : 0.42 amps.per Sq.dm.
Duration of electrolysis : 30 minutes.

Obs. No.	Electrode distance Cms.	Wt.of copper deposited in coulometer gms.	Wt.of tin deposited gms.	CCE %	(Mean)	Nature of deposit.
1	2	0.026	0.043	87.78	(87)	Bright fine.
		0.032	0.051	54.58		
2	*+4	0.029	0.049	89.67	(88)	Bright fine with silvery shining.
		0.031	0.050	85.60		
3	6	0.030	0.049	86.68	(87)	-do-
		0.030	0.049	86.68		
4	8	0.030	0.049	86.68	(87)	-do-
		0.030	0.050	89.40		
5	10	-	-	-		-do-

* Optimum condition.   + cf. Plate 9.

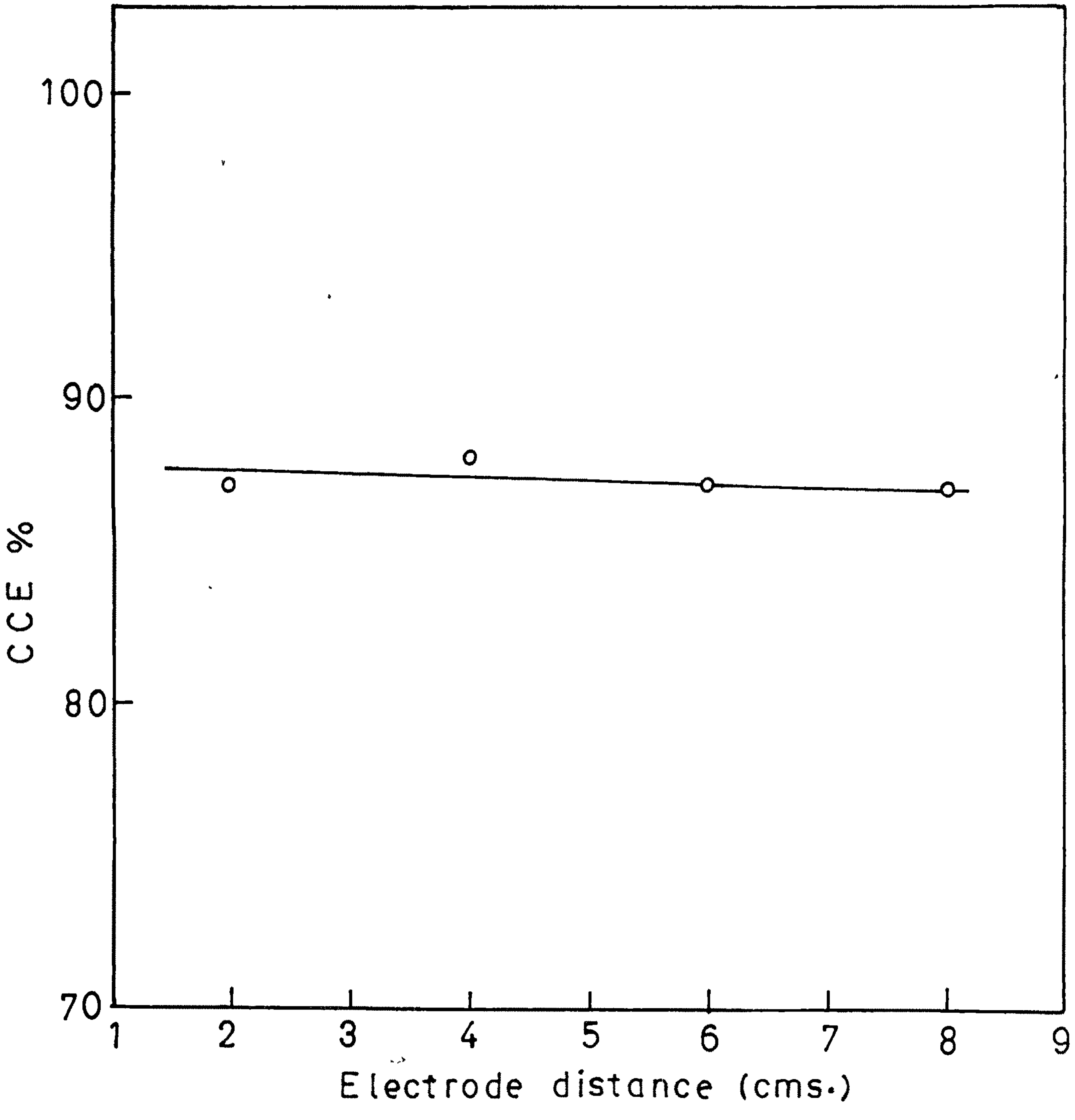


Fig. 15 — Effect of electrode distance on cathode current efficiency (CCE %) of Tin deposit.

TABLE NO.16 :- The effect of addition agents on the metal content and the percentage cathode current efficiency (CCE %) of tin deposit.

Tin chloride : 4 gms.per 100 ml.
Sodium chloride : 4 gms.per 100 ml.
Temperature : 30°C.
Electrode distance : 4 Cms.

Hydrochloric acid : 0.8 N in mixture
Current density : 0.42 amps.per Sq.dm.
Duration of electrolysis : 30 minutes.
Voltage : 1 Volt.

Ser. No.	Addition agent	Amount of addition agent per 100 ml. gms.	Wt. of copper deposited in coulometer gms.	Wt. of tin deposited gms.	CCE %	(Mean)	Nature of deposit.
1	Glucose	0.3 gms.	0.024	0.043	95.08	(94)	Good, but considerable tree formation.
			0.025	0.044	93.40		
2	Sugar	0.3 gms.	0.024	0.044	97.30	(96)	Good, tree formation tendency less than previous.
			0.025	0.045	95.53		
3	Carbon di-sulphide	.1 ml.	-	-	-		Black, non-adherent.
4	+ Agar-Agar powder.	0.3 gms.	0.027	0.047	92.38	(92)	Very fine, bright, lustrous and uniform. No tree formation at all.
			0.025	0.043	91.28		
5	Gelatine	0.3 gms.	0.025	0.045	95.53	(97)	Adherent, bright, fine and uniform. No tree formation.
			0.025	0.046	97.65		
6	Gum Arabica	0.3 gms.	0.025	0.040	93.89	(92)	- do -
			0.027	0.048	90.43		
7	Acetone	.1 ml.	0.025	0.046	95.51	(97)	Fine grained, bright, very slight tree formation at edges.
			0.025	0.046	97.65		

cf. Plate 10.

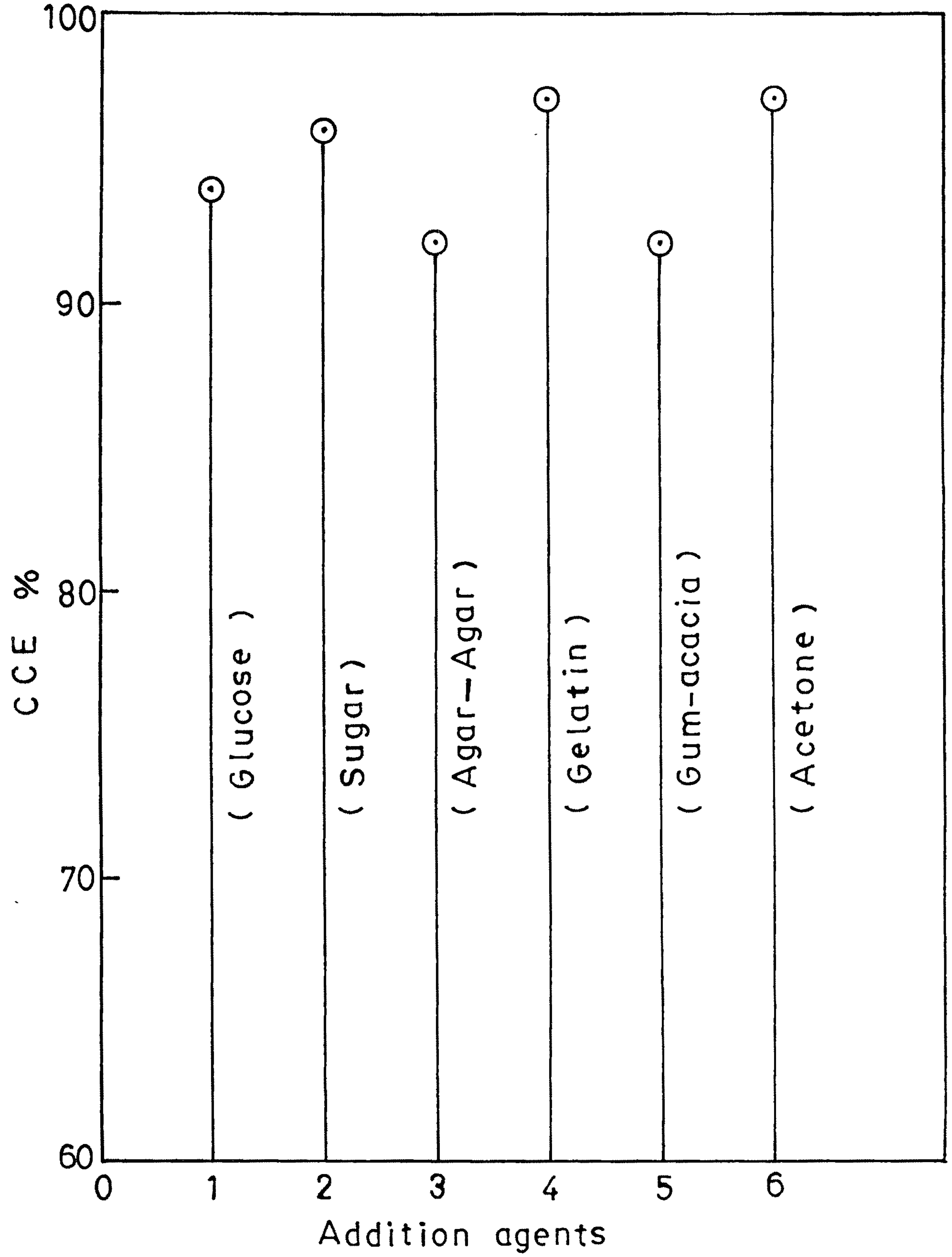


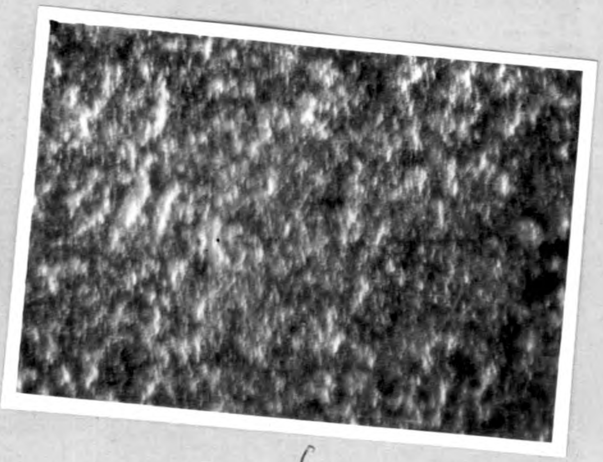
Fig. 16—Effect of addition agents on cathode current efficiency (CCE %) of Tin deposit.

SUMMARY

TIN SYSTEM (OPTIMUM CONDITIONS)

Table 16-A : The influence of the Physico-chemical factors, upon the nature and magnitude of the tin deposit has been shown in the previous Table Nos. 9 to 16 and graphically in Figs.9 to 16.The ranges over which parameters were and optimum conditions arrived at by experiments, are summerised below:

Parameter studied and Range	Optimum condition
1) Composition of the bath	-
a)Concn.of tin chloride 2-8 gms. per 100 ml of the solution.	4 gms.per 100 ml of the solution.
b)Concn.of hydrochloric acid 0.4 to 1.6 Normal (Normality in mixture).	0.8 N (Normality in mixture).
c)Concn.of sodium chloride 2 to 6 gms per 100 ml of the solution.	4 gms.per 100 ml of the solution.
2) Current density 0.084 -1.04 amps per Sq.dm.	0.42 amps.per sq.dm.
3)Temperature 10°-50°C	30°C.
4) Duration of Electrolysis 10-50 minutes.	30 minutes.
5) Electrode distance 2 - 10 cms.	4 cms.



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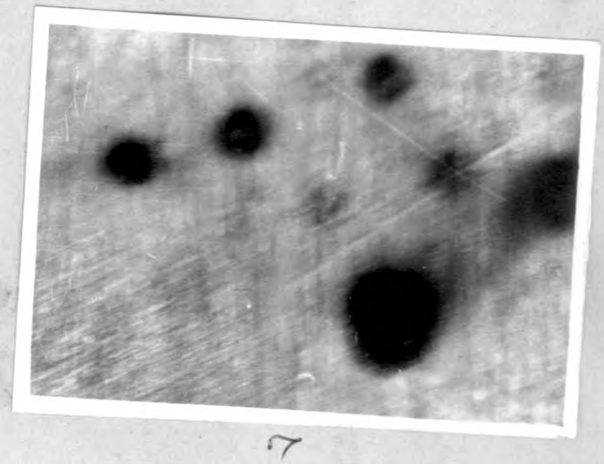

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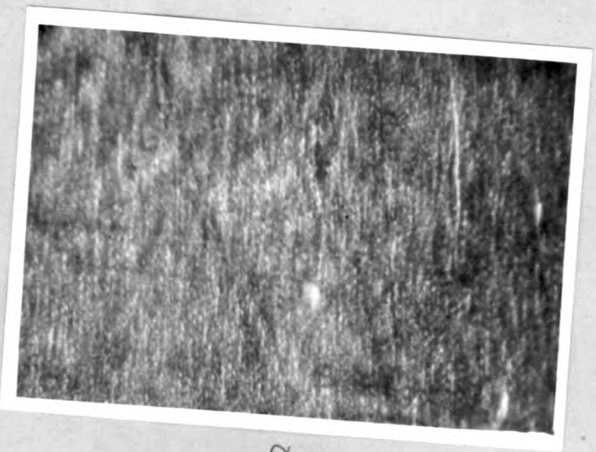

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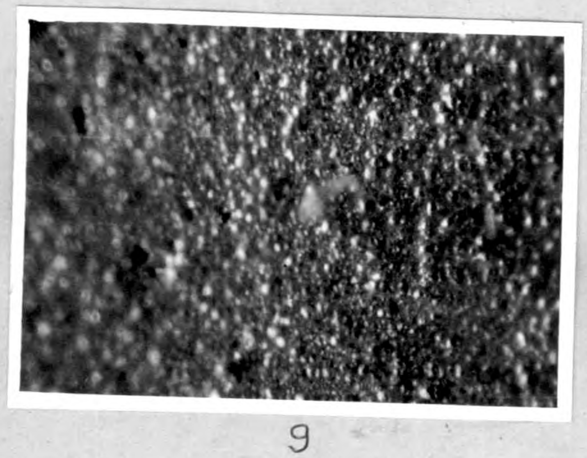

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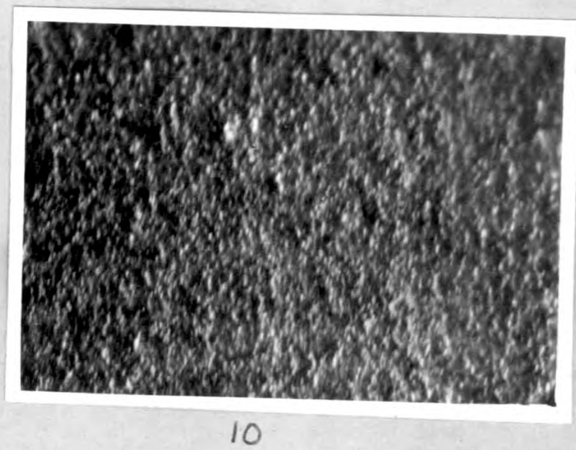

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cf.plate 6-10 (Tin)

3.5 Results and Discussion (Table 9-16, Figs 9-16) for Tin :

The influence of different parameters on composition of the deposit, cathode current efficiency (CCE), structure and appearance of the deposits have been detailed below :

EFFECT OF ELECTROLYTE CONCENTRATION :

1) Effect of tin chloride concentration (Cf Table-9, Fig-9) :

The composition of tin chloride in the bath was varied from 2 to 0 gms per 100 ml in the bath. It was found that increase in the conc. of tin chloride in the bath improved the quality of the deposit. At low concentration, treeing effect was observed, but as concentration was increased, no treeing was seen. There was also an increase in the CCE with increase in the concentration of tin chloride, however, the amount of tin deposited nearly remained constant. Fine adherent and shining deposits were obtained at 4 gms. of tin chloride per 100 ml of solution.

2) Effect of Hydrochloric acid concentration (Cf. Table-10, Fig - 10) :

The bath used for tin deposition was hydrochloric acid bath. The acid bath has the advantage that the valence of tin in it is II compared with IV in the stannate bath; hence twice as tin is deposited, at 100 % efficiency per ampere-hour in the acid as in the alkaline bath. The cathode efficiency is usually about 95 percent in the acid bath and may be only 75 %

in the alkaline bath. This was actually the case observed. The CCE observed was above 85 % in general. From Table - 10, it was observed that, at 0.8 N concentration of hydrochloric acid, the deposits obtained were fine, adherent and shining. However, at higher concentrations, there was evolution of hydrogen gas near cathode.

3) Effect of Sodium chloride concentration (Cf Table-11, Fig - 11) :

Concentration of sodium chloride was changed between 2-5 gms per 100 ml. The quality and nature of the deposit was found to be improved with increasing concentration of sodium chloride and lustrous, smooth, uniform and adherent deposits were obtained at 4 gms. per 100 ml. This might be probably due to increased conductivity of the bath. The composition and CCE of the metal content were found to decrease with increase in the concentration of sodium chloride. At higher concentrations the deposits were not satisfactory due to evolution of hydrogen.

4) Effect of current density (Cf Table 12 Fig - 12) :

Current densities ranging from 0.084 - 1.04 amps per Sq. dm. were used. At low C.D. the deposits were nonadherent and unsatisfactory. The quality of deposits improved as C.D. was increased upto 0.42 amps. per Sq.dm. At 0.42 amps per sq.dm., the deposits obtained were quite satisfactory, but further increase of C.D. resulted in increase in the tree formation tendency. At high C.D. nonadherent deposits were obtained.

with increase in C.D., tin content and CCE of the deposit were increased to a great extent.

5) Effect of temperature (Cf Table 13, Fig - 13) :

The temperature range studied was 10°- 50°C, under optimum condition of both composition and C.D. The tin content in the deposit decreased with increase in temperature. The quality of the deposits was found to be satisfactory at 30°C. (Optimum condition), but beyond this temperature no improvement was observed. At higher temperature (50°C) it became inferior.

6) Effect of duration of electrolysis (Cf Table -14, Fig-14):

Electrolysis was carried out for 10-15 minutes under otherwise optimum condition. Change in the deposit composition was not appreciable with respect to the duration of electrolysis. The CCE decreased steadily. The deposits were bright uniform, and aderent at 30 minutes (optimum condition), but little tree formation tendency was observed, as duration of electrolysis was increased to more than 30 minutes.

7) Effect of electrode distance (Cf Table -15, Fig.15):

The distance between anode and cathode was changed between 2-10 cms. It was noticed that the character of the deposit as well as the composition and CCE, were not affected.

8) Effect of addition agents (Cf Table 16, Fig - 16) :

A number of addition agents were added seperately and singly to the bath under optimum conditions and the results are summarised in Table - 16. It was found that brighter and smoother deposits were obtained in presence of Agar Agar powder, Gelatine and Gum-Arabica. For glucose, sugar and acetone there observed the tree formation tendency, although the quality of deposits was good. However for carbon di-sulphide the deposits obtained were black and nonadherent.

3·6 Role of Complexes in Electrodeposition of Zinc and Tin :

It is worth wise to discuss the fine character of the deposit on the basis of complexes that are believed to be formed in the respective baths, selected for Zn and Sn deposition. The deposition of metals, according to Gnee , is a crystal growth process. It consists initially of the formation of nuclei at the cathode surface followed by their growth to larger crystals. The two processes occur simultaneously with different velocities. If the rate of nuceli formation is more than the crystal growth, the deposit obtained is fine grained whereas if the crystal growth is more rapid, it favours cluster formation and the deposit is coarse, non-uniform and unsatisfactory.

Composition of the bath has marked effects on the relative velocities of nuclei formation and on their subsequent crystal growth. The cathode polarization and the structure of the deposit also play their own role. It would appear that for the production of a rapid and thick deposit, the presence of a large number of metallic ions in the electrolytic is desirable. But this would favour rather the rapid growth of a few crystals than the production of a large number of small crystals, which is the characteristic of a fine grained deposit. On the other hand if dilute solutions are used, the passage of a current soon removes the metal ions present near the cathode and burnt, spongy deposits results. Agitation of the solution would bring the other metal ions nearer to the cathode but at the same time it stirs the sludge that is invariably found at the bottom of the bath. This precipitate settle on the cathode and makes the deposit rough and uneven. Hence the use of dilute solutions with agitation is not desirable. Therefore, an ideal bath composition (electrolyte concentration) would be one containing a few metal ions but plenty of dissolved metal salt to furnish a fresh supply of ions as fast as they are removed. The solution of a complex salt of the metal satisfies this condition. The complex ionises in two or more stages, the metal usually being ionised at the last stage and to a limited extent. This means that the rate of formation of nuclei is actually decreased by increasing the concentration of the dissolved metal salt in presence of a ligand like alkali thiocyanide added in the bath. The ions are made available for discharge at the cathode as and when required and thus a uniform adherent deposit would result. The resulting complexes containing largely the zinc metal ions in the form of $Zn(CN)_2$ or $Zn(\overline{CNS})_3$ and others hitherto unknown, might get formed. Thio-cyanide ions are bound up with zinc. We have however ~~so~~ no specific evidence for the formation of different types of complexes to attain equilibrium. As such we have to depend on the meagre data available with us indicating the formation of the following types of complexes with known instability constants , one for overall complex and the others for stepwise dissociation complexes.

The high sulphocyanide concentration gives maximum conductivity and also provides largely as a complexing ion in solubilising Zn $(CNS)_2$, forming complex salts of probable compositions. The most important variables in controlling the formation of specific complexes are the pH and the thiocyanate content of the bath. The complexes of the types mentioned may be supposed to dissociate as follows :

Zn- Complexes (Thiocyanate bath) :

The reactions that are believed to occur may be summarised as follows :

$$ZnSO_4 + 2KCNS = \overset{*}{Zn}(CNS)_2 + K_2SO_4 \quad \ldots (1)$$

or

$$Zn^{2+} + 2KCNS = \overset{*}{Zn}(CNS)_2 + 2K^{+} \quad \ldots (2)$$

$$Zn(CNS)_2 \quad Zn^{2+} + 2\,\overline{CNS} \quad \ldots (3)$$

* Equilibrium or Dissociation constant being not very low (about 10^{-10}) may yield a complex Zn $(\overline{CNS})_3$ as follows :

$$Zn(CNS)_2 + KCNS = Zn(CNS)_3^{-} + K^{+} \quad \ldots (4)$$

$$Zn\,(\overline{CNS})_3 = Zn^{2+} + 3\,CNS^{-} \quad \ldots (5)$$

Zn^{2+} either from (3) or (5) gets reduced at the cathode

$$Zn^{2+} + 2\overline{e} = Zn^{0}(Solid) \quad \ldots (6)$$

The further growth of deposit follows the laws of adsorption. Bare parts of the cathode are deposited by fresh metal ions for their turn to be discharged.

Tin Complexes (Acid Chloride Bath) :

The reactions that are believed to occur may be summarised as follows :

Stannous and Stannic Complexes :

$SnCl_2 + 2\,NaCl = Na_2SnCl_4$ ... Soluble salt ..(1)

OR

$SnCl_2 + 4\,NaCl = Na_4SnCl_6$ .. -do- ..(2)

$Na_4SnCl_6 = 4Na^+ + SnCl_6^{4-}$ (Complex) ..(1A)

$SnCl_6^{4-} = Sn^{2+} + 6Cl^-$ ..(1A)′

OR

$Na_2SnCl_4 = 2Na^+ + SnCl_4^{2-}$ (Complex) ..(2A)

$SnCl_4^{2-} = Sn^{2+} + 4\,Cl^-$ ..(2A)′

Sn^{2+} produced from feeble dissociation of the complex as in (1A)′ or (2 A)′, gets reduced at the cathode as :

$Sn^{2+} + 2\bar{e} = Sn^0(s)$

Alternatively, as the bath ages and the stannous tin oxidises, higher complexes due to the availability of d orbitals, get formed and the coordination number increases from four to six. Thus, stannic complexes may be envisaged.

$SnCl_4 + 2NaCl = Na_2SnCl_6$ (solubilisation)

$Na_2SnCl_6 = 2\,Na^+ + SnCl_6^{2-}$ (complete dissociation)

$SnCl_6^{2-} = Sn^{4+} + 6Cl^-$ (Complex feebly dissociating)

$Sn^{4+} + 4\bar{e} = Sn^0$ (s)