

CHAPTER 3

ELECTRODEPOSITION OF SINGLE METALS

(Zinc and Tin)



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 ($\text{pH} = 7$) the potential for the reversible evolution of hydrogen would be -

$$\mathcal{E}_{\text{H}_2} = 1.0 - \frac{0.059}{1} \log \frac{1}{10^{-7}} = -0.61 \text{ volt.}$$

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 Cu (-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 fluoroborate 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, so 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 efficiencies 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 increases the cathode efficiency.

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

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

- 1) ^{con}
^ Concentration of the electrolytes,
- 2) Current density,
- 3) Temperature,
- 4) Duration of electrolysis,
- 5) Electrode distance,
- 6) Additive 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 :

Cyanide 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 recognized and bath composition not too early postwar years by porotor and Wenlund (28) and Blum et al (29). Developmental highlights include the introduction by splinger (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 fluoroborates, acid septic acid sulphate, alkaline zincate or alkaline cyanide type is described by Martin sylvia and co-workers (33). Similarly Buchette, 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 No. 2 : The effect of concentration of zinc sulphate on the total current and the percentage current efficiency (Case A) of the zinc deposit.
 Potassium hydroxide : 5 gms per 100 ml. Total current : 1 amp. over 100 ml.
 Temperature : 30° C. Current density : 1.66 amp. per 100 cm.
 Duration of electrolysis : 20 minutes
 Zinc sulphate : 5 gms per 100 ml. Blockage current : 1.66 amp. per 100 cm.
 Voltage : 1.07 to 1.12 v.

| No. of bathes | Concentration of zinc sulphate (gms. per 100 ml) | Type of copper electrode | Current (amp.) | Current efficiency (%) | Nature of deposit | |
|---------------|--|--------------------------|----------------|------------------------|-------------------|--|
| | | | | | (Mean) | (Case A) |
| 1 | 5 | | 0.065 | 0.024 | 35.91 (33) | Pure and adherent, blocky at the edges. |
| | | | 0.066 | 0.028 | 40.00 (33) | |
| 2 | 10 | | 0.066 | 0.029 | 42.15 (41) | Uniform good, adherent and white bright. |
| | | | 0.076 | 0.031 | 39.69 (41) | |
| 3 | 15 | | — | — | — | Not so good but quite adherent. |
| | | | — | — | — | Bloody, non-adherent and black. |
| 4 | 20 | | 0.068 | 0.036 | 51.01 (52) | — |
| | | | 0.067 | 0.037 | 52.21 (52) | — |
| 5 | 30 | | 0.077 | 0.037 | 59.36 (61) | — |
| | | | 0.075 | 0.046 | 62.46 (61) | — |
| 6 | 40 | | 0.082 | 0.052 | 60.17 (63) | — |
| | | | 0.082 | 0.062 | 69.66 (63) | — |

* Optimum condition.

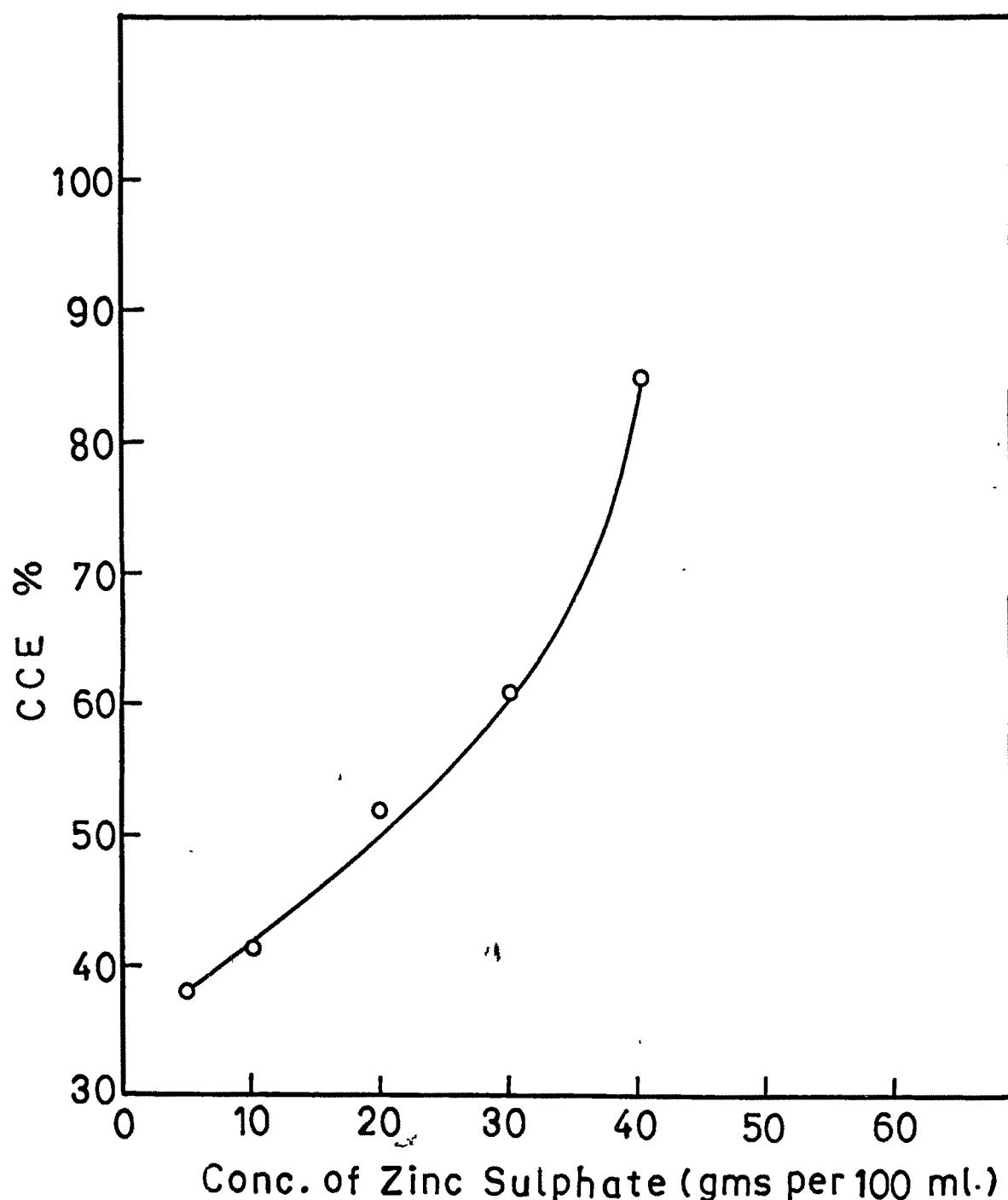


Fig. 1—Effect of Zinc Sulphate concentration on cathode current efficiency (CCE %) of Zinc deposit .

TABLE 130.2 THE EFFECT OF CONCENTRATION OF ROTATING ELECTRODE ON THE METAL CONTENT AND THE PERCENTAGE COPPER EFFICIENCY (SCS AT 1% OF THE CUPROUS DEPOSIT).

Mine sulphate = 10 gms. per 100 ml.
Current density = 1.5 amp per 50 cm.
Concentration of electrolyte = 10 minutes
Voltage = 1.0 to 1.2 volts.

| No. | Percentage of cupro- copper deposited per 100 ml. | Nature of deposit | Not satisfactory (full deposit) | | Uniform deposit and bright | Uniform deposit in irregular | Good deposit but necessitating re-treatment | as three processes. | Adherent but non-uniform | and scratchy.* |
|-----|---|-------------------|---------------------------------|-----------------|----------------------------|------------------------------|---|---------------------|--------------------------|----------------|
| | | | at 100% current | at 200% current | | | | | | |
| 1 | 1 | - | - | - | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| 2 | 5 | 0.024 | 35.91 | 40.00 | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| 3 | 10 | 0.023 | 35.91 | 40.00 | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| 4 | 15 | 0.024 | 35.91 | 40.00 | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| 5 | 20 | 0.024 | 35.91 | 40.00 | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| 6 | 25 | 0.025 | 35.91 | 40.00 | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |
| | | | | | | | | | | |
| | | | | | 35.91 | (30) | 37.64 | (37.0) | 37.05 | (37.0) |

* Optimum condition.

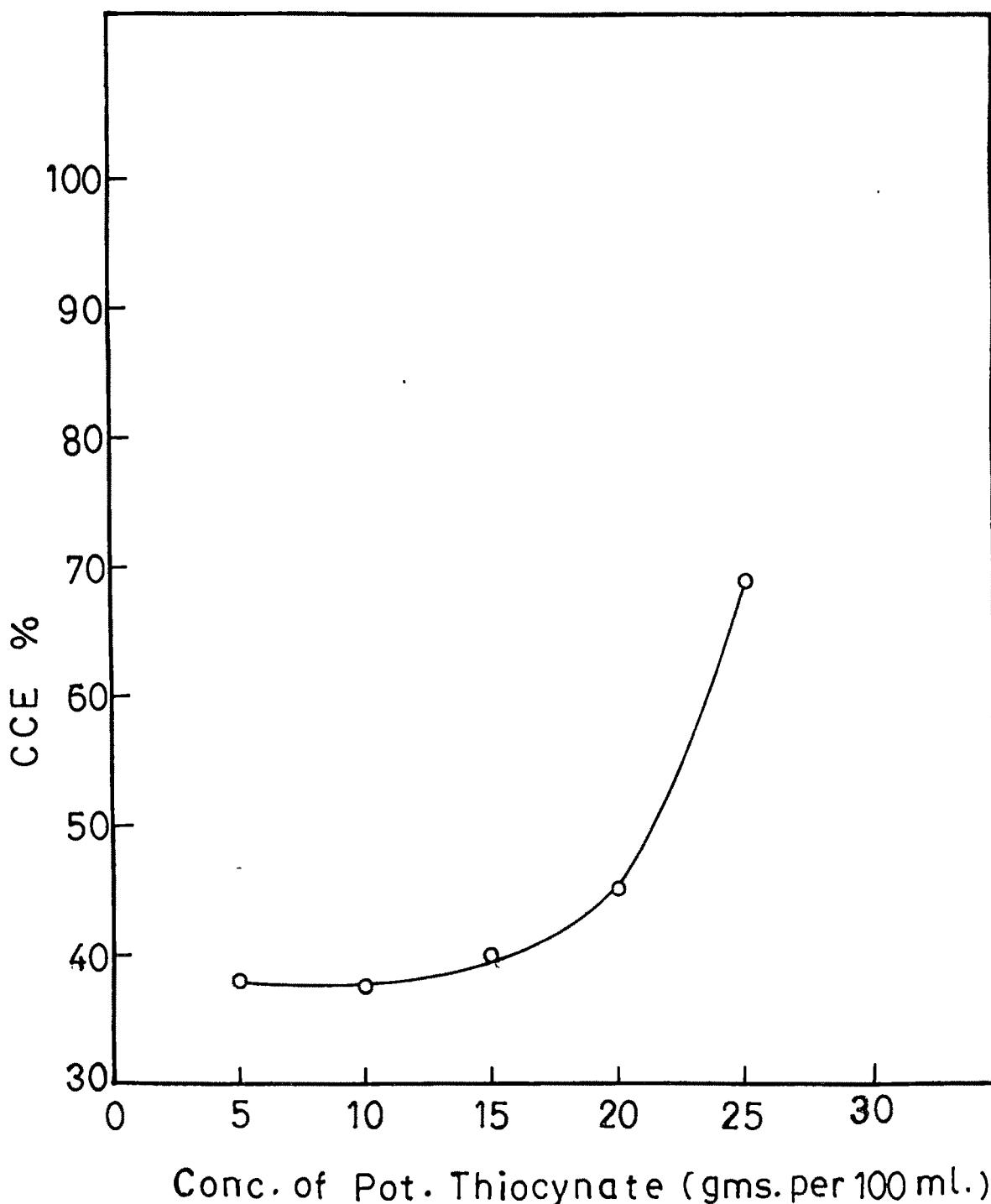


Fig.2 — Effect of Potassium Thiocyanate concentration
on cathode current efficiency (CCE %)
of Zinc deposit .

| | | | |
|---------------------------------------|---------|---------------------------------|---------|
| Zinc sulphate + 10 gms. | 100 ml. | Potassium thiocyanate + 10 gms. | 100 ml. |
| Current density : 1.5 amp per sq. cm. | | Temperature : 30 °C. | |
| Duration of electrolysis : 20 minutes | | Electrode distance : 4 cm. | |
| Thickness of deposit : 2 mm. | | | |

| Number of samples | | Percentage | | Nature of sample. | | Number of samples | | Percentage | | Nature of sample. | |
|-------------------|-------|------------|-------|-------------------|-------|-------------------|-------|------------|-------|-------------------|-------|
| Specie | Genus | Specie | Genus | Specie | Genus | Specie | Genus | Specie | Genus | Specie | Genus |
| 1 | 1 | 0.035 | 0.035 | 2 | 2 | 0.034 | 0.034 | 3 | 4 | 0.032 | 0.032 |
| 2 | 2 | 0.036 | 0.036 | 4 | 4 | 0.032 | 0.032 | 5 | 5 | 0.030 | 0.030 |
| 3 | 3 | 0.034 | 0.034 | 6 | 6 | 0.031 | 0.031 | 7 | 7 | 0.029 | 0.029 |
| 4 | 4 | 0.031 | 0.031 | 8 | 8 | 0.028 | 0.028 | 9 | 9 | 0.027 | 0.027 |
| 5 | 5 | 0.031 | 0.031 | 10 | 10 | 0.026 | 0.026 | 11 | 11 | 0.025 | 0.025 |
| 6 | 6 | 0.031 | 0.031 | 12 | 12 | 0.025 | 0.025 | 13 | 13 | 0.024 | 0.024 |
| 7 | 7 | 0.031 | 0.031 | 14 | 14 | 0.024 | 0.024 | 15 | 15 | 0.023 | 0.023 |
| 8 | 8 | 0.031 | 0.031 | 16 | 16 | 0.023 | 0.023 | 17 | 17 | 0.022 | 0.022 |
| 9 | 9 | 0.031 | 0.031 | 18 | 18 | 0.022 | 0.022 | 19 | 19 | 0.021 | 0.021 |
| 10 | 10 | 0.031 | 0.031 | 20 | 20 | 0.021 | 0.021 | 21 | 21 | 0.020 | 0.020 |
| 11 | 11 | 0.031 | 0.031 | 22 | 22 | 0.020 | 0.020 | 23 | 23 | 0.019 | 0.019 |
| 12 | 12 | 0.031 | 0.031 | 24 | 24 | 0.019 | 0.019 | 25 | 25 | 0.018 | 0.018 |
| 13 | 13 | 0.031 | 0.031 | 26 | 26 | 0.018 | 0.018 | 27 | 27 | 0.017 | 0.017 |
| 14 | 14 | 0.031 | 0.031 | 28 | 28 | 0.017 | 0.017 | 29 | 29 | 0.016 | 0.016 |
| 15 | 15 | 0.031 | 0.031 | 30 | 30 | 0.016 | 0.016 | 31 | 31 | 0.015 | 0.015 |
| 16 | 16 | 0.031 | 0.031 | 32 | 32 | 0.015 | 0.015 | 33 | 33 | 0.014 | 0.014 |
| 17 | 17 | 0.031 | 0.031 | 34 | 34 | 0.014 | 0.014 | 35 | 35 | 0.013 | 0.013 |
| 18 | 18 | 0.031 | 0.031 | 36 | 36 | 0.013 | 0.013 | 37 | 37 | 0.012 | 0.012 |
| 19 | 19 | 0.031 | 0.031 | 38 | 38 | 0.012 | 0.012 | 39 | 39 | 0.011 | 0.011 |
| 20 | 20 | 0.031 | 0.031 | 40 | 40 | 0.011 | 0.011 | 41 | 41 | 0.010 | 0.010 |
| 21 | 21 | 0.031 | 0.031 | 42 | 42 | 0.010 | 0.010 | 43 | 43 | 0.009 | 0.009 |
| 22 | 22 | 0.031 | 0.031 | 44 | 44 | 0.009 | 0.009 | 45 | 45 | 0.008 | 0.008 |
| 23 | 23 | 0.031 | 0.031 | 46 | 46 | 0.008 | 0.008 | 47 | 47 | 0.007 | 0.007 |
| 24 | 24 | 0.031 | 0.031 | 48 | 48 | 0.007 | 0.007 | 49 | 49 | 0.006 | 0.006 |
| 25 | 25 | 0.031 | 0.031 | 50 | 50 | 0.006 | 0.006 | 51 | 51 | 0.005 | 0.005 |
| 26 | 26 | 0.031 | 0.031 | 52 | 52 | 0.005 | 0.005 | 53 | 53 | 0.004 | 0.004 |
| 27 | 27 | 0.031 | 0.031 | 54 | 54 | 0.004 | 0.004 | 55 | 55 | 0.003 | 0.003 |
| 28 | 28 | 0.031 | 0.031 | 56 | 56 | 0.003 | 0.003 | 57 | 57 | 0.002 | 0.002 |
| 29 | 29 | 0.031 | 0.031 | 58 | 58 | 0.002 | 0.002 | 59 | 59 | 0.001 | 0.001 |
| 30 | 30 | 0.031 | 0.031 | 60 | 60 | 0.001 | 0.001 | 61 | 61 | 0.000 | 0.000 |
| 31 | 31 | 0.031 | 0.031 | 62 | 62 | 0.000 | 0.000 | 63 | 63 | - | - |
| 32 | 32 | 0.031 | 0.031 | 64 | 64 | 0.000 | 0.000 | 65 | 65 | - | - |
| 33 | 33 | 0.031 | 0.031 | 66 | 66 | 0.000 | 0.000 | 67 | 67 | - | - |
| 34 | 34 | 0.031 | 0.031 | 68 | 68 | 0.000 | 0.000 | 69 | 69 | - | - |
| 35 | 35 | 0.031 | 0.031 | 70 | 70 | 0.000 | 0.000 | 71 | 71 | - | - |
| 36 | 36 | 0.031 | 0.031 | 72 | 72 | 0.000 | 0.000 | 73 | 73 | - | - |
| 37 | 37 | 0.031 | 0.031 | 74 | 74 | 0.000 | 0.000 | 75 | 75 | - | - |
| 38 | 38 | 0.031 | 0.031 | 76 | 76 | 0.000 | 0.000 | 77 | 77 | - | - |
| 39 | 39 | 0.031 | 0.031 | 78 | 78 | 0.000 | 0.000 | 79 | 79 | - | - |
| 40 | 40 | 0.031 | 0.031 | 80 | 80 | 0.000 | 0.000 | 81 | 81 | - | - |
| 41 | 41 | 0.031 | 0.031 | 82 | 82 | 0.000 | 0.000 | 83 | 83 | - | - |
| 42 | 42 | 0.031 | 0.031 | 84 | 84 | 0.000 | 0.000 | 85 | 85 | - | - |
| 43 | 43 | 0.031 | 0.031 | 86 | 86 | 0.000 | 0.000 | 87 | 87 | - | - |
| 44 | 44 | 0.031 | 0.031 | 88 | 88 | 0.000 | 0.000 | 89 | 89 | - | - |
| 45 | 45 | 0.031 | 0.031 | 90 | 90 | 0.000 | 0.000 | 91 | 91 | - | - |
| 46 | 46 | 0.031 | 0.031 | 92 | 92 | 0.000 | 0.000 | 93 | 93 | - | - |
| 47 | 47 | 0.031 | 0.031 | 94 | 94 | 0.000 | 0.000 | 95 | 95 | - | - |
| 48 | 48 | 0.031 | 0.031 | 96 | 96 | 0.000 | 0.000 | 97 | 97 | - | - |
| 49 | 49 | 0.031 | 0.031 | 98 | 98 | 0.000 | 0.000 | 99 | 99 | - | - |
| 50 | 50 | 0.031 | 0.031 | 100 | 100 | 0.000 | 0.000 | 101 | 101 | - | - |

cf plate 1

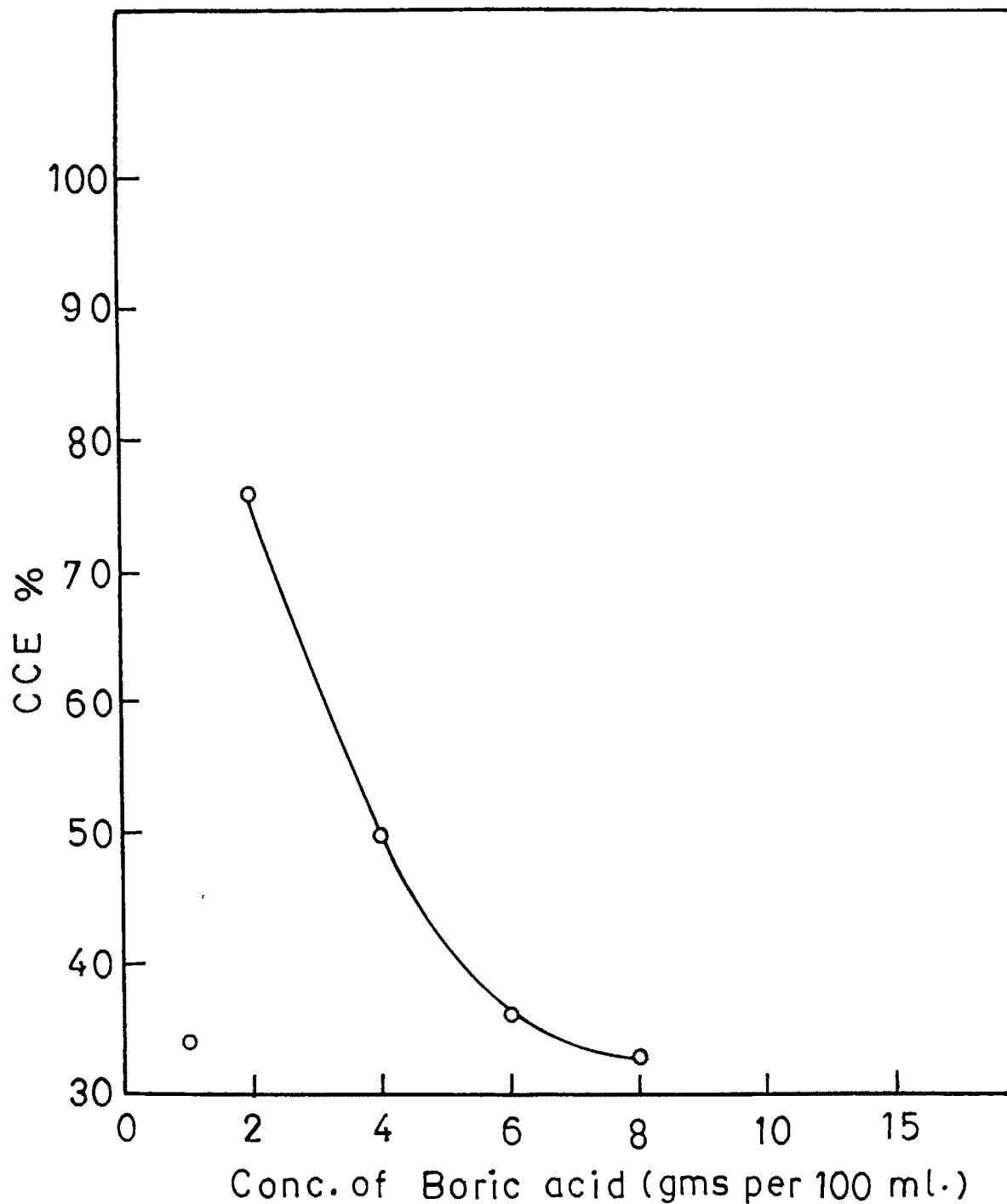


Fig.3—Effect of Boric acid concentration on cathode current efficiency (CCE %) of Zinc deposit .



TABLE IV - The effect of current density on the metal content and the percentage cathode current efficiency (η_{eff} %) of the zinc deposit.

Zinc sulphate : 10 gms. per 100 ml.
Sonic field : 2 gms. per 100 ml.
Current of electrolysis : 20 amperes
Voltage : 1.9 to 2 volts.
 η_{eff} : 100%.

| Cath. Current Amp. No. | Current density amp./per cm. ² | Wt. of copper deposited gm. | Wt. of zinc deposited gm. | Percentage of zinc deposit. | Nature of deposit. | Percentage of zinc deposit. | |
|------------------------------|--|-----------------------------------|------------------------------------|-----------------------------------|---|-----------------------------------|-----|
| | | | | | | (%) | (%) |
| 1. | 0.3 | 0.032 | 0.012 | 36.12 | Spatchy with black spot, unsatisfactory. | (38) | |
| | | 0.030 | 0.013 | 41.76 | | | |
| 2. | 1.6 | 0.066 | 0.032 | 46.72 | One black spot, bright and smooth deposit. | (47) | |
| | | 0.064 | 0.033 | 49.63 | | | |
| 3. | 2.4 | 0.081 | 0.031 | 60.87 | Delightful, brilliant, uniform, golden green. | (60) | |
| | | 0.079 | 0.031 | 61.42 | | | |
| 4. | 3.2 | 0.127 | 0.083 | 62.97 | Smooth but slightly black. | (64) | |
| | | 0.125 | 0.072 | 66.07 | | | |
| 5. | 4.0 | 0.130 | 0.113 | 63.76 | Unsatisfactory. Spotty nonuniform. | (62) | |
| | | 0.134 | 0.114 | 61.97 | black with tracing at edges. | | |

* Optimum condition.
+ cf Plate 2

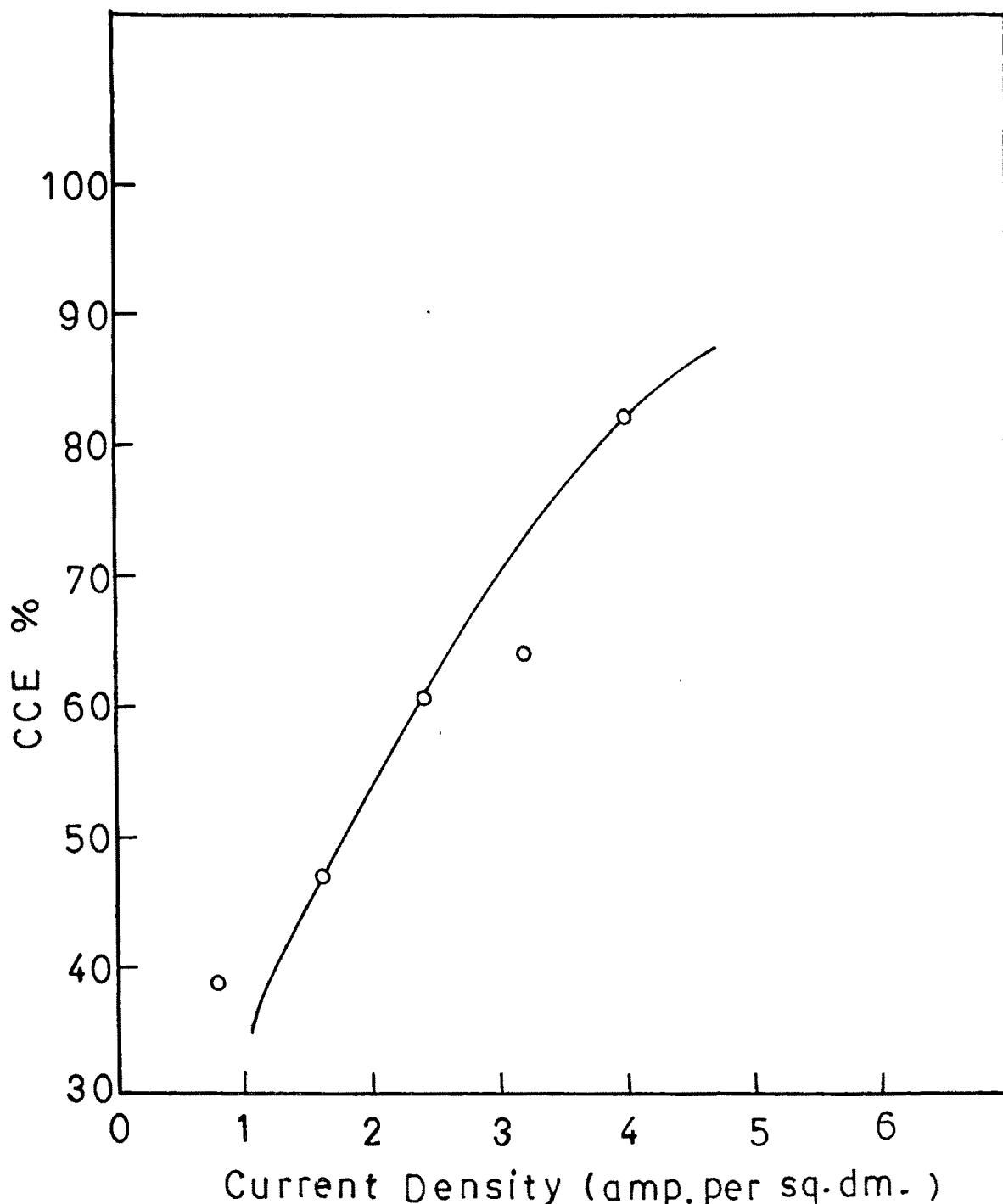


Fig. 4.—Effect of current density on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO. 5 - The effect of temperature (°C.) on the metal content and the percentage cathode current efficiency (%) of the zinc deposit.

Zinc anode : 10 gms. per 100 ml.
Tetrasodium thiocyanate : 10 gms. per 100 ml.
Sulfuric acid : 2 gms. per 100 ml.
Current density : 2.4 amp. per 50 cm.
Molar ratio of electrolyte : 20 molar.
Electrode distance : 4 cms.
Voltage : 2 volts.

| No. | Temp. °C. | Cath. of copper deposited in cu. cm. gms. | Percentage of current efficiency | | Comment on deposit |
|-----|--------------|---|---|--|--|
| | | | Cath. of zinc deposited in cu. cm. gms. | Percentage of current efficiency | |
| 1 | 10 | 0.054 | 0.041 | 73.03 (73) | Non uniform but adherent. |
| | | 0.055 | 0.041 | 72.69 | |
| 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 | 67.35 (68) | Smooth bright and adherent. |
| | | 0.066 | 0.033 | 69.00 | |
| 4 | 40 | 0.064 | 0.026 | 39.13 (40) | Smooth surface but slightly blistered. |
| | | 0.065 | 0.027 | 40.00 | |
| 5 | + 50 | 0.061 | 0.020 | 65.68 (44) | Rough and rough surface. |
| | | 0.062 | 0.027 | 42.36 | Very brittle structure. |

* Optimum condition.
** Plate 3.

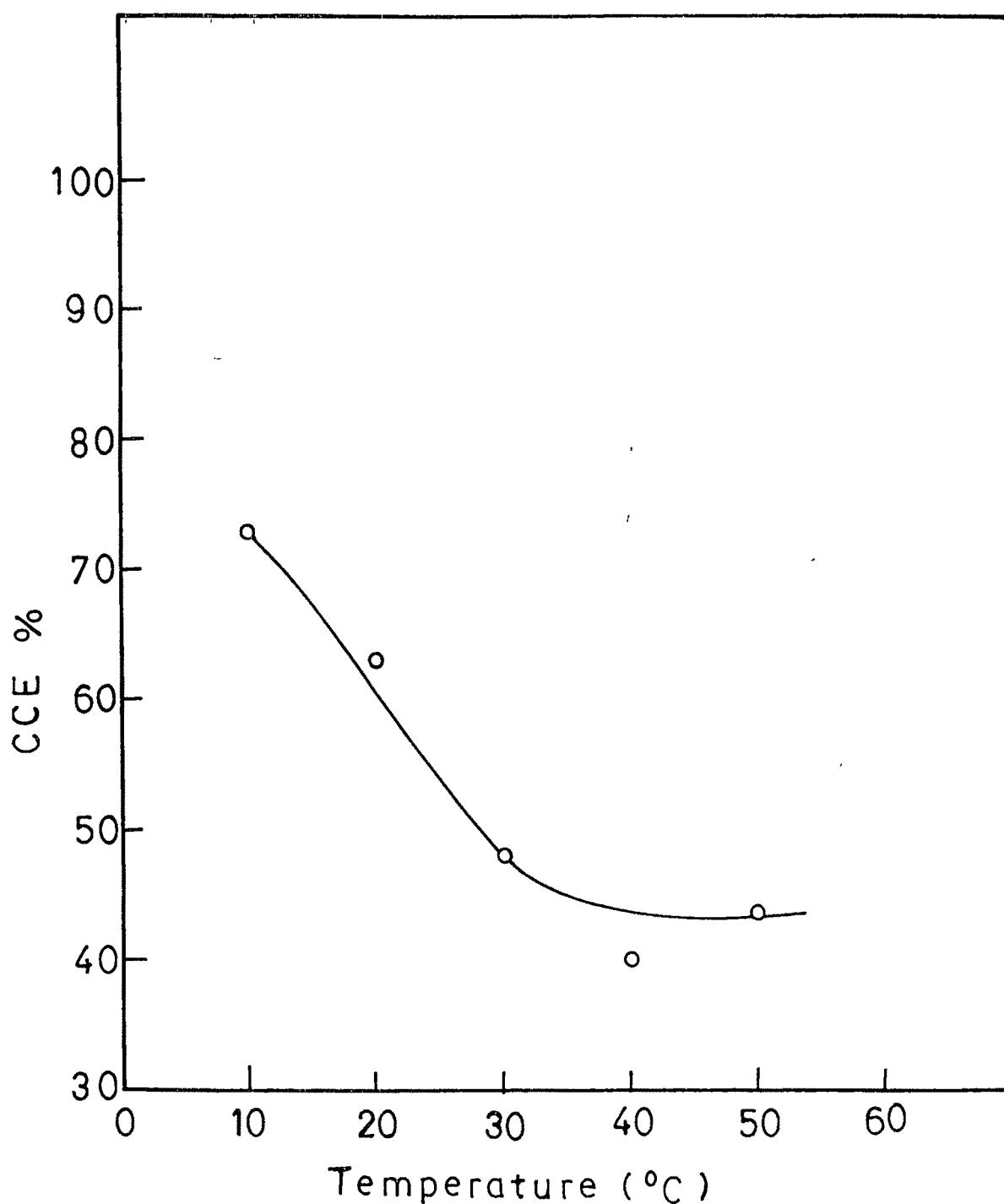


Fig. 5—Effect of temperature on cathode current efficiency (CCE %) of Zinc deposit.

TABLE NO. 6 - The effect of duration of electrolysis on the total content and the percentage of cathode current efficiency (C.C.E.) of the zinc deposit.

Zinc sulphate : 10 gms. per 100 ml. **Vaseline** (electrolyte) : 10 gms. per 100 ml.
Boric acid : 2 gms. per 100 ml. Current density : 2.4 amp. per sq. dm.
Electrode distance : 4 cms.
Voltage : 2 volt.

| No. | Duration of electrolysis in hours | Current intensity amp. | Concentration of zinc deposit gms. | Nature of deposit. | |
|-----|---|------------------------------|---|--------------------|--|
| 1 | 6 | 0.035 | 0.015 | 41.30 (40.0) | Smooth impure. |
| 2 | 10 | 0.036 | 0.015 | 62.66 (69) | Smooth but slightly impure. |
| 3 | 15 | 0.037 | 0.017 | 63.8 | Smooth and good. |
| 4 | 20 | 0.037 | 0.017 | 63.76 (82) | With granules & slightly grainy. |
| 5 | 20 | 0.037 | 0.017 | 63.59 (84) | - 60 - Blackish powder found to be adsorbed on the cathode. |

* Optimum conditions.

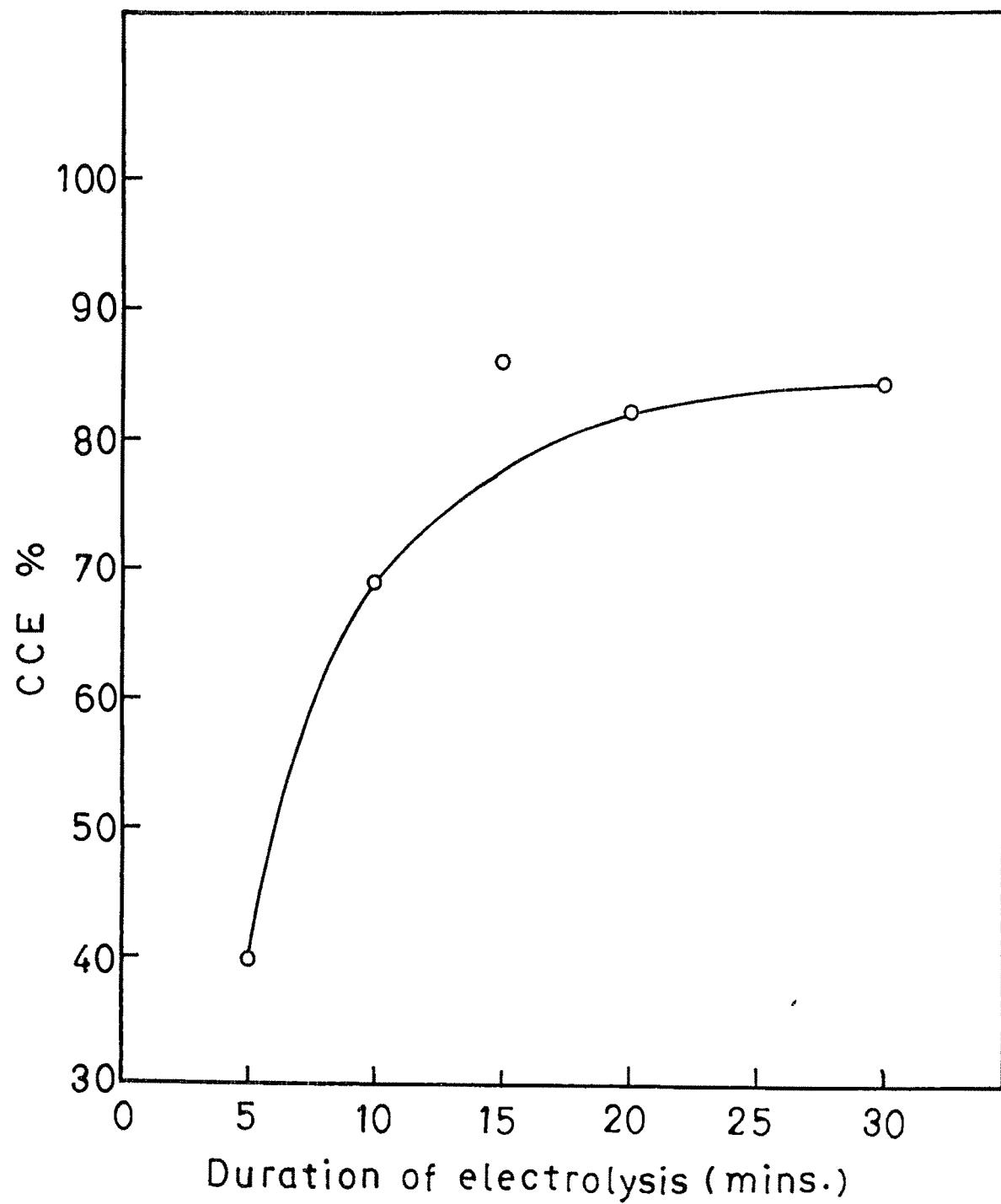


Fig. 6 — Effect of duration of electrolysis on cathode current efficiency (CCE %) of Zinc deposit .

the first time since 1945, the Japanese government has been compelled to apologize for its actions during the Second World War.

10 AUGUST 1922.

+ Cf Plate 4.

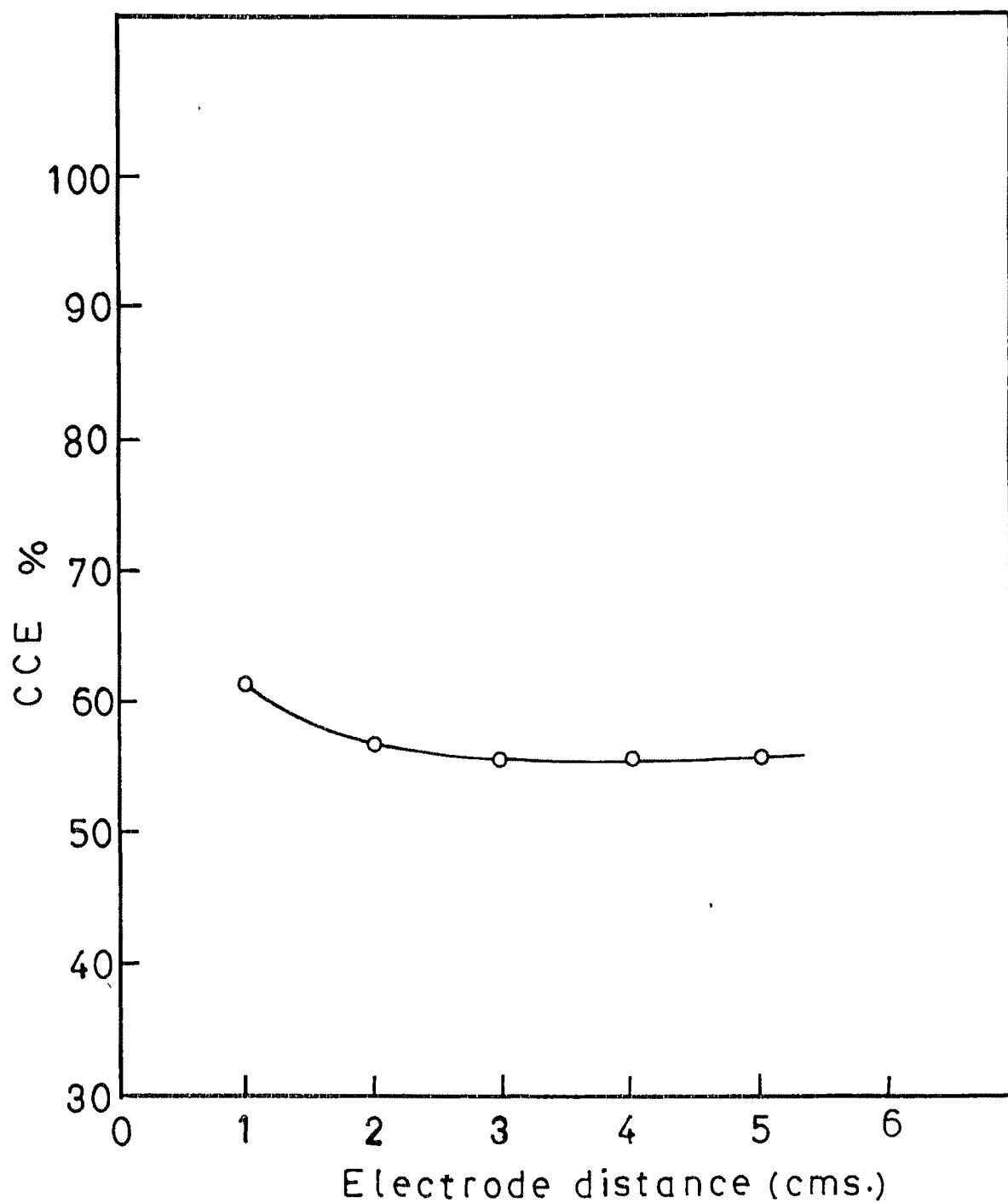


Fig. 7 — Effect of electrode distance on cathode current efficiency (CCE %) of Zinc deposit .

FIGURE 10. Effect of addition of agents on the initial content and the percentage eroded.

Water bath temp. 30 °C. per 100 ml. Temperature bath temp. 30 °C. per 100 ml.
Sonic bath 2 °C. per 100 ml. Temperature bath temp. 30 °C. per 100 ml.
Temperature : 30 °C. per 100 ml. Voltage : 2 Volts.

No. Agent No. of cycles of bath
per 100 ml. Composed in
gas. Gas.

No. Agent No. of cycles of bath
per 100 ml. Composed in
gas. Gas.

No. Agent No. of cycles of bath
per 100 ml. Composed in
gas. Gas.

| No. | Agent | No. of cycles of bath per 100 ml. | Composed in gas. | No. of cycles of bath per 100 ml. | Composed in gas. | No. of cycles of bath per 100 ml. | Composed in gas. |
|-----|-----------------|--------------------------------------|---------------------|--------------------------------------|---------------------|--------------------------------------|---------------------|
| 1 | Hyde | 0.3 | 0.050 | 0.020 | 0.054 (30.0) | 0.020 | 0.036 (22.0) |
| 2 | Codamine | 0.3 | 0.050 | 0.021 | 0.047 (40.0) | 0.021 | 0.035 (22.0) |
| 3 | Camphor | 0.3 | 0.053 | 0.022 | 0.049 (40.0) | 0.022 | 0.036 (22.0) |
| 4 | + Camphor | 0.3 | 0.057 | 0.021 | 0.057 (40.0) | 0.021 | 0.035 (22.0) |
| 5 | Camphor - 1 ml. | 0.3 | 0.051 | 0.020 | 0.057 (40.0) | 0.020 | 0.035 (22.0) |
| 6 | Hyde | 0.327 | 0.051 | 0.025 | 0.055 (40.0) | 0.025 | 0.035 (22.0) |
| 7 | Camphor - 1 ml. | 0.327 | 0.053 | 0.025 | 0.057 (40.0) | 0.025 | 0.035 (22.0) |
| 8 | Hyde | 0.327 | 0.053 | 0.025 | 0.057 (40.0) | 0.025 | 0.035 (22.0) |

+ CF plate 5

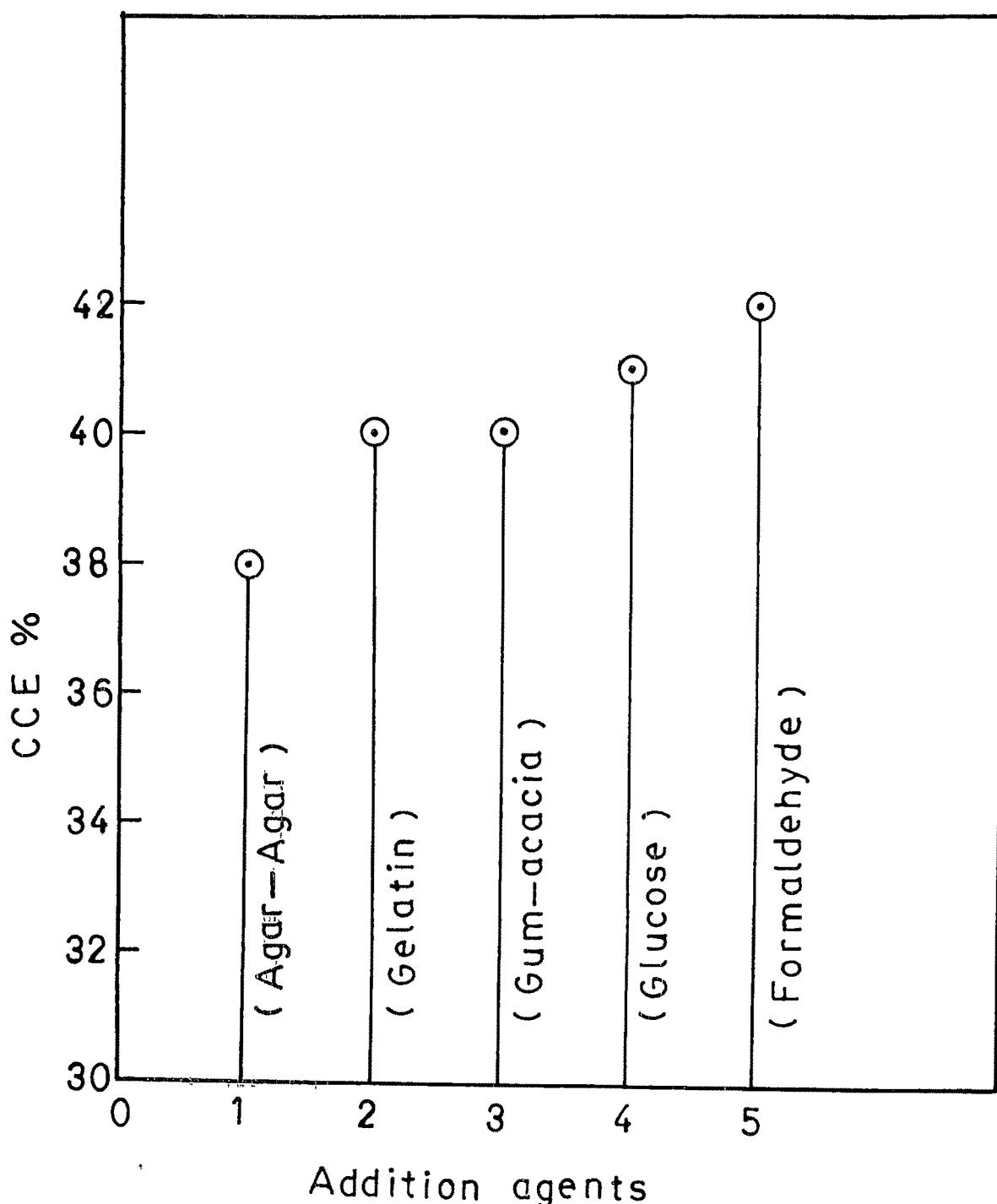


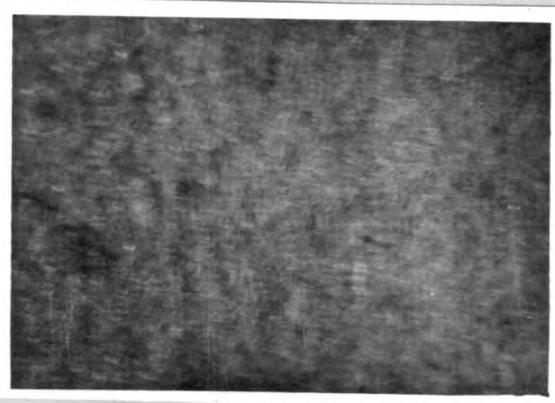
Fig. 8 — Effect of addition agents on cathode current efficiency (CCE %) of Zinc deposit .

5212
A

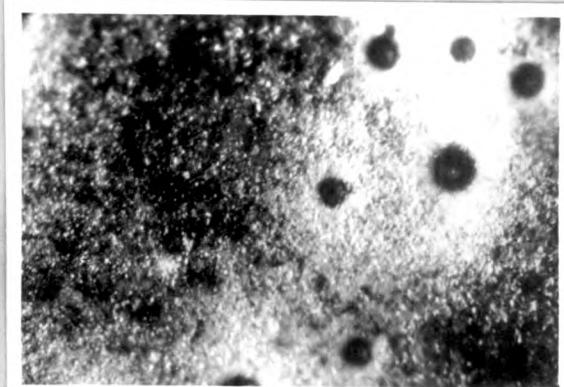
SUMMARYZinc System (Optimum Conditions)

Table 88: 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:

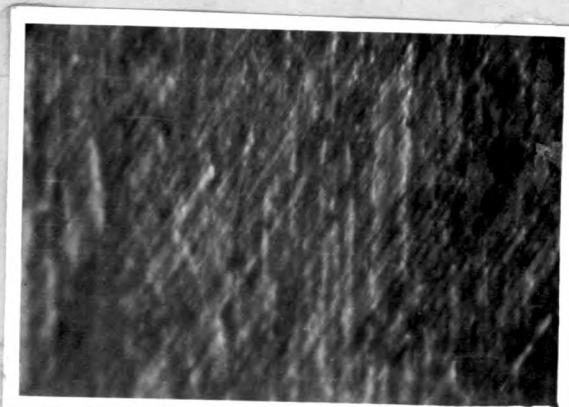
| Parameters studied and Range | Optimum condition |
|---|--------------------------------------|
| 1) Composition of the bath. | - |
| a)Concn. of zinc sulphate 5-40 gms per 100 ml. of the solution. | 10 gms. per 100 ml. of the solution. |
| b)Concn. of Potassium thiocyanate 1-25 gms per 100 ml. of the solution. | 10 gms. per 100 ml. of the solution. |
| c)Concn. of Boric acid 1-6 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. | 2.4amps. 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. |



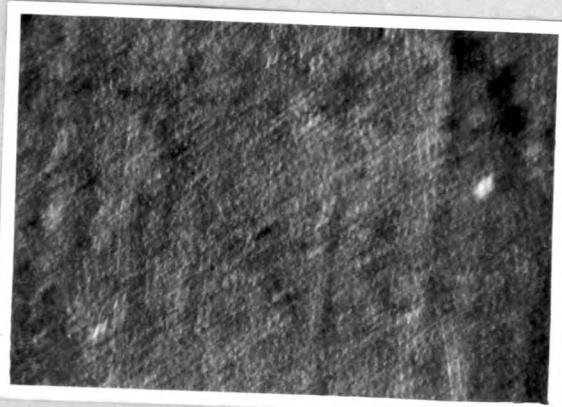
1



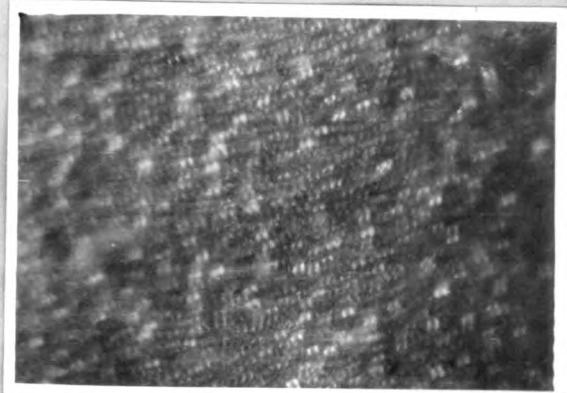
2



3



4



5

c.f. plate 1-5 (Zinc)

GARR. BALASAHEB KHARDEKAR LIBRARY
SHIVAJI UNIVERSITY, KOLHAPUR

3.3 Results and Discussion for Zinc + (Table I-3, Fig 1-3)

The plating variables had a marked effect on the quality and composition of the deposits and also on the O.C.E. The effects of different variables are explained below :

Effect of Zinc Sulphate Concentration :

1) Effect of Zinc Sulphate Concentration : (See 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 deposits with increase in the concentration of zinc sulphate. At the same time Z.D 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 thiocyanate concentration (See table 2, Fig.2) :

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

1 gms 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 blocking of the deposit occurs as time proceeds. Side by side tracking 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 GCD. The optimum condition was obtained at 10 gms. of potassium thiocyanate per 100 ml.

3) Effect of Boric acid concentration (Cf. Table - 3, Fig - 3) :

Boric acid has a marked effect on the nature of deposit and especially on GCD. With increase in the concentration of Boric acid, the GCD 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) Effect of Current Density (Cf. Table - 4, Fig - 4) :

Using a bath of optimum composition, current densities varying from 0.0 to 4.0 A/cm² were studied. In the lower region of current density (0.0 A/cm²), the deposits were dull, closely and patchy but with an increase in current density upto 2.4 A/cm² , fine grained more shining and adherent deposits,

were obtained. Above this current density, the deposits turned black and showed bulging effect (4.0 A/cm^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, η_{ad} also increases. The optimum condition for current density was 2.4 A/cm^2 , when the deposit obtained was bright and uniform.

3) Effect of temperature : (see Table - 3, Fig. 5) :

An increase in temperature in general, decreases the polarisation of the more noble metal relatively more than the polarisation of the less noble metal and causes an increase in the crystal size. The temperature range studied was 10°C - 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), salt

and rough deposit was produced, zinc content in the deposit and its ZIR decreased proportionately with an increase in the temperature.

The optimum condition obtained for temperature was 30°C.

6) Effect of duration of electrolyte (See Table 6 Fig - 6) :

Under optimum conditions, the period of electrolyte 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. ZIR also changed from 40 to 84%, thus with decrease in duration ZIR 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 condition was that of 15 minutes.

7) Effect of variation of electrode distance (See Table-7, Fig - 7) :

The electrode distance between anode and cathode was changed between 1.0 - 5 cm. It was noticed that the character of the deposit as well as the composition and ZIR, 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.

9) Effect of addition agents (Cf. Table - 6, Pg - 6) :

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 favorable effect upon the deposits. 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 these 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 size remained more or less the same.

3.4 Electrodeposition of Tin from Acid Chloride Bath:

Methods for the electrodeposition of tin, from either acid sulphate or alkaline solutions, have been known for more than 100 years. Horwood 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 stannite (ex Na_2SnO_3). The most important difference in these baths is the greater throwing power of the alkaline stannite baths, however the acid bath has the advantage that the valence of tin in it is II, compared with IV in the stannite 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 reversed 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, commercially

known as the "Ferration" and "Halogen" processes, respectively, have achieved worldwide 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 fluoroborate and halogen formulations are in common use.

In 1942 the Grasselli post organization, in response to request from welspun 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 Schwellner, Hoffmann, and Grey et al (59) formed the original basis for the "Halogen Tin" process. A review by Du Rose (60) of the early developments of the process indicates that the transition from pilot plant to full scale production at a speed of 330 m/min was achieved in one year. Much credit goes to Grasselli research team and the welspun 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 ZSE (over 90 %) even on copper, iron and other base metals. The bath is easy to handle, and gives good reproducibility of results.

3.4: | 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. Mathews and co-workers (61) tested many of these early baths and found them satisfactory. Proctor (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 Freine were apparently the first to publish a plating bath based on sodium stannate. As far as acidic 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).

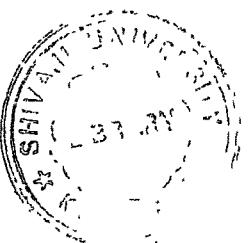
Research on tin electrodeposition continued at a rapid pace after 1960. Numerous articles and patents have appeared in the literature describing new addition agents, brightness, crystal structure, effect of temperature, throwing power etc. (65 to 70).

TABLE NO. 9-i - The effect of concentration of the tin chloride on the metal content and the percentage cathodic current efficiency (see Fig. 1) of the tin deposit.

Deposition rate: 1.2 gm. per minute.
Current density: 0.725 A./dm².
Concentration of electrolyte: 30 gms./dm³.
Voltage: 1 volt.

| OBS. No. | Concentrations of tin deposited in cathode area gm. dm ⁻² | % of copper deposited in cathode area gm. dm ⁻² | Rate of tin deposited gm. dm ⁻² | | % of tin deposit (mean) | Nature of deposit as per formation. |
|-------------|---|--|---|------------|----------------------------------|--|
| | | | No. 1 | No. 2 | | |
| 1 | 0.032 | 0.052 | 86.75 | 86.75 (96) | 86.53 | Uniform, coherent with 1.25 cm. ESR no formation. |
| 2 | 0.035 | 0.051 | 85.83 | 85.83 (96) | 85.83 | Uniform and coherent. No tin formation. |
| 3 | 0.038 | 0.049 | 87.60 | 87.60 (96) | 87.55 | Uniform and coherent. No tin formation. |
| 4 | 0.040 | 0.048 | 81.50 | 81.50 (96) | 81.45 | Uniform, coherent. No tin formation. |

* Current densities.



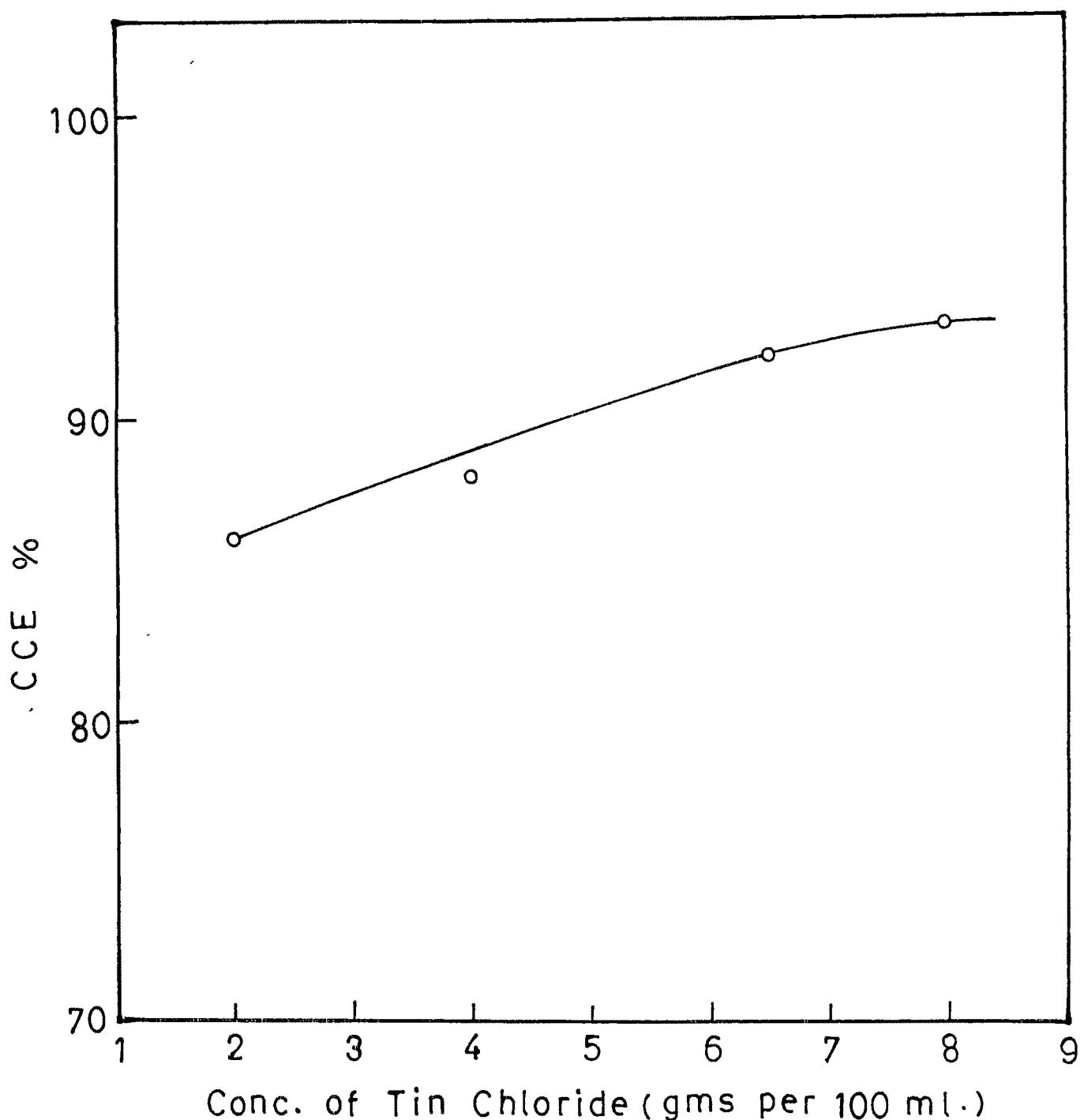


Fig.9—Effect of Tin Chloride concentration on cathode current efficiency (CCE %) of Tin deposit .

* Optimum conditions.

TABLE II - The effects of concentrations of hydrogenated oil on the initial content and the percentages of hydrocarbon substances in the oil droplets.
 Sun oil/cetene = 6 parts, total 100 ml. Sulfur content 0.2%, 2 ppm. Total 100 ml.
 Current density = 0.72 ampere/cm². Temperature = 20°C.
 Treatment of electrolyte = 30 minutes. Resistance distance = 6 cm.
 Voltage = 1 volt.

| Concen- tration of hydro- genated oil (ppm) | Initial content of hydro- carbon substances (%) | | | Final content of hydro- carbon substances (%) | | |
|---|---|----------|---------------------------------------|---|----------|---------------------------------------|
| | Cetene | Paraffin | Hydro- cyclic hydro- carbons | Cetene | Paraffin | Hydro- cyclic hydro- carbons |
| 0.0 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 1 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 2 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 3 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 4 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 5 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 6 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 7 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 8 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 9 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 10 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 11 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 12 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 13 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 14 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 15 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 16 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 17 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 18 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 19 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 20 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 21 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 22 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 23 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 24 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 25 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 26 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 27 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 28 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 29 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 30 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 31 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 32 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 33 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 34 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 35 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 36 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 37 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 38 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 39 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 40 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 41 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 42 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 43 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 44 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 45 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 46 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 47 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 48 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 49 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 50 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 51 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 52 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 53 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 54 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 55 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 56 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 57 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 58 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 59 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 60 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 61 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 62 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 63 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 64 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 65 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 66 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 67 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 68 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 69 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 70 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 71 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 72 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 73 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 74 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 75 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 76 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 77 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 78 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 79 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 80 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 81 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 82 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 83 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 84 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 85 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 86 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 87 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 88 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 89 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 90 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 91 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 92 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 93 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 94 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 95 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 96 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 97 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 98 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 99 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |
| 100 | 9.00 | 8.00 | 8.00 | 9.00 | 8.00 | 8.00 |

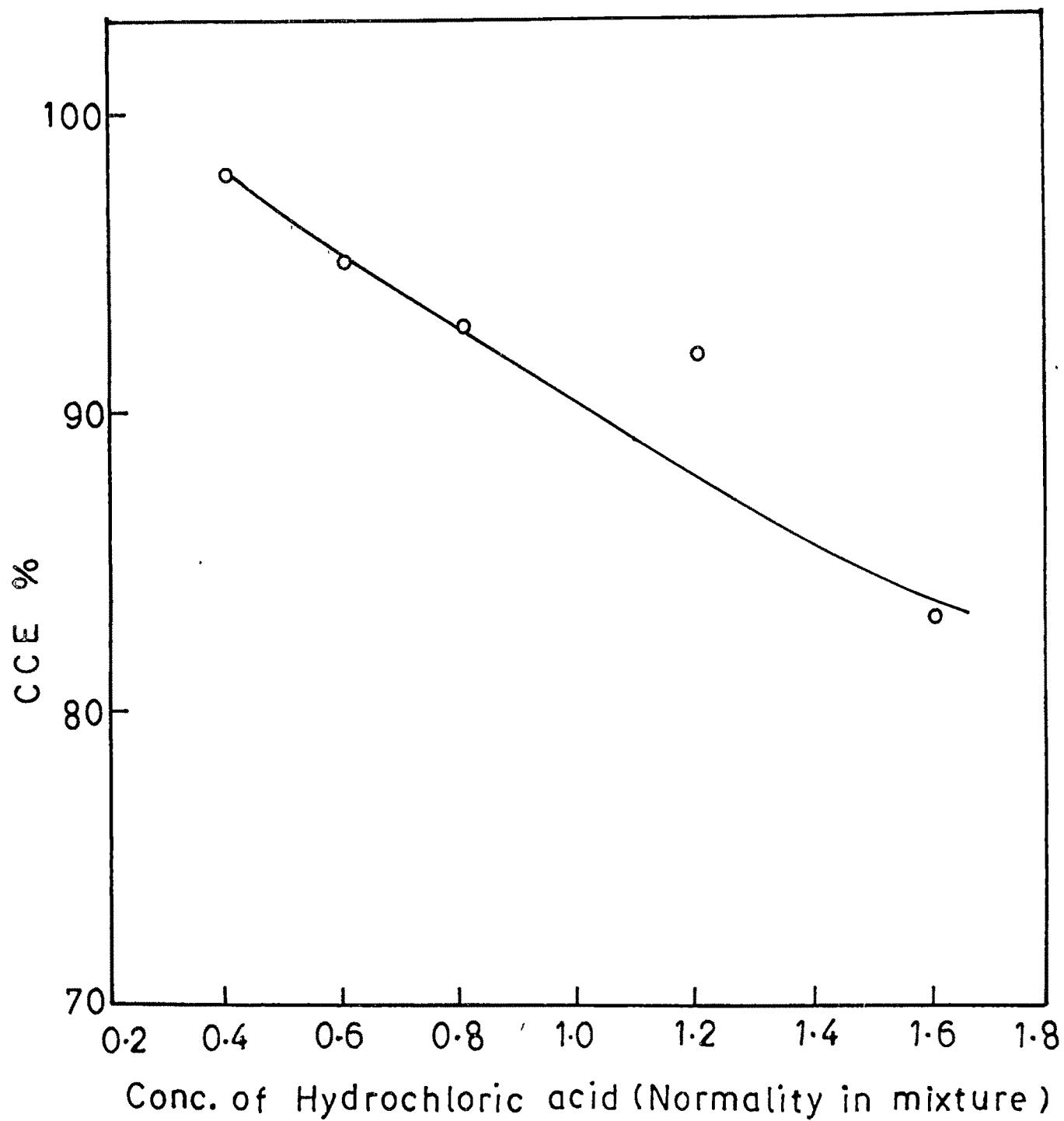


Fig. 10 —Effect of Hydrochloric acid concentration on cathode current efficiency(CCE %) of Tin deposit.

The effect of concentration of specific chlorides on the total content of free chlorine was measured by the iodine method with 0.01 N iodine solution. The percentage change of chlorine content at different concentrations of specific chlorides is given in Table I.

卷之三

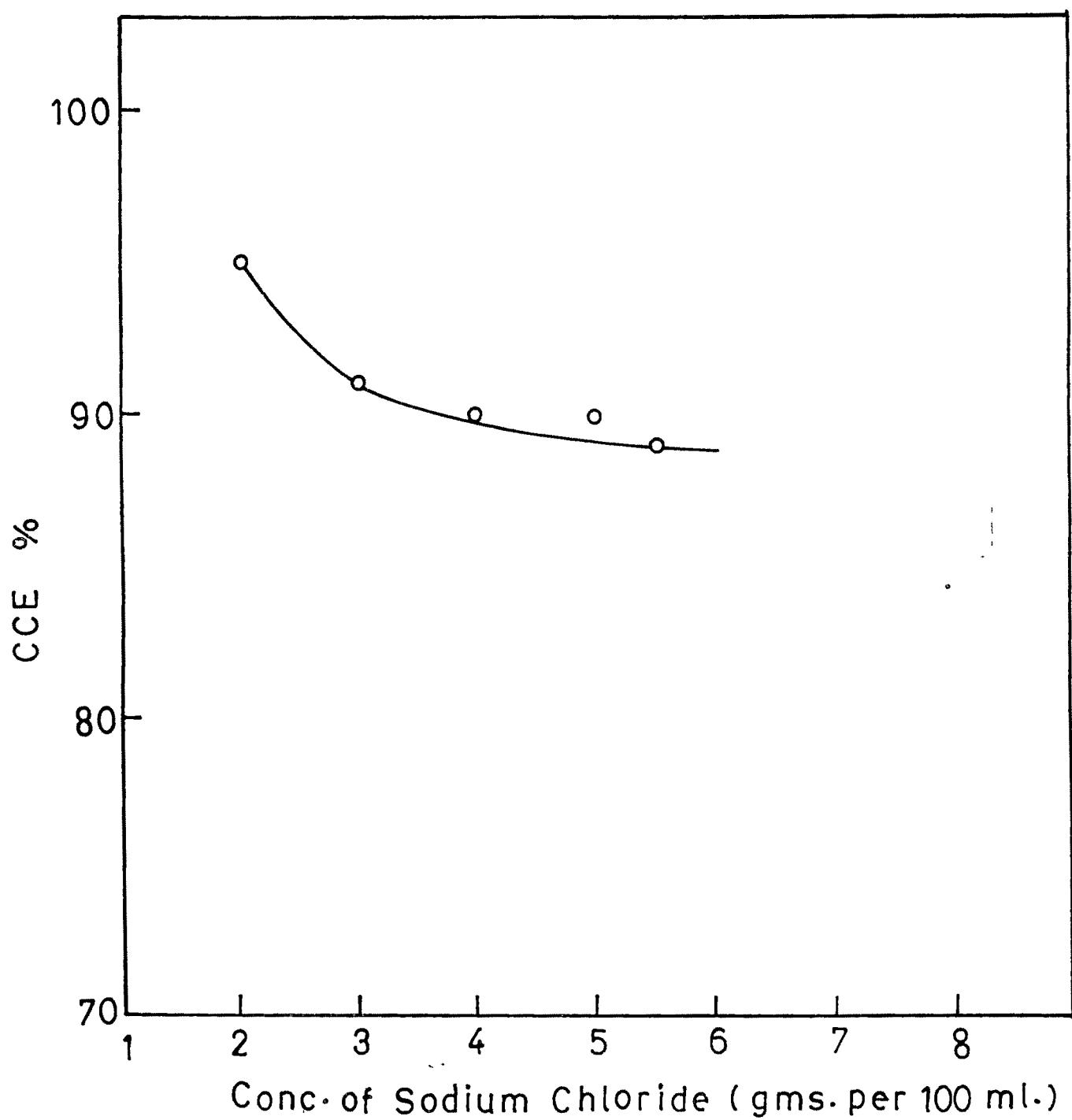


Fig. 11 — Effect of Sodium Chloride concentration on cathode current efficiency(CCE %) of Tin deposit .

प्राप्ति एवं ये विषयों का अध्ययन विभिन्न विधियों के द्वारा किया जाता है।

the other side of the river, and the two sides of the valley were covered with dense woods.

Optimal condition.
+ cf plate 6.

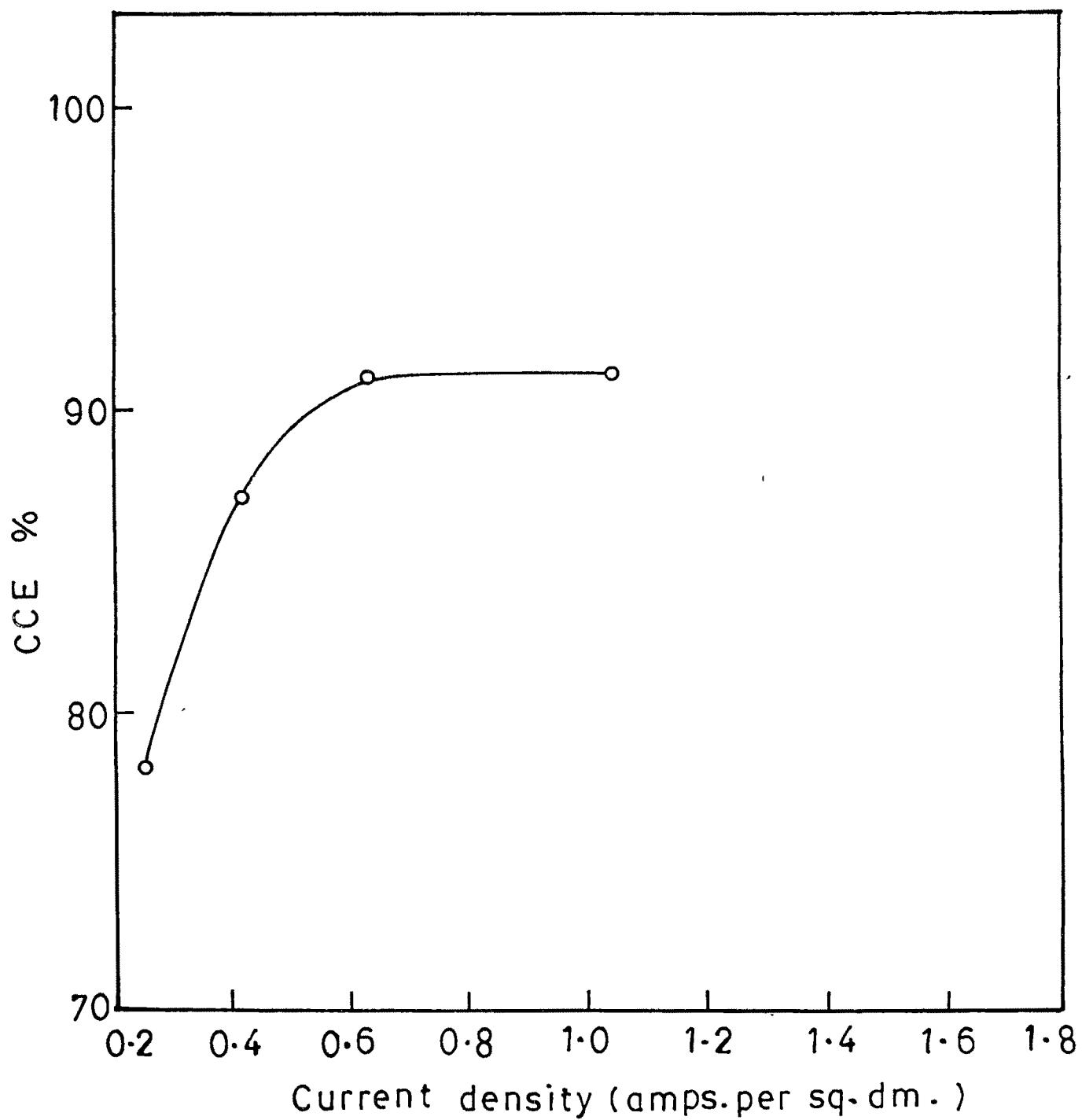


Fig.12 – Effect of current density on cathode current efficiency (CCE %) of Tin deposit .

Figures 10-12 show the effect of temperature on the metal content and the percentage extraction of tellurite (Te₂O₅) of tin dioxide. Tin dioxide is granular, 100 ml. solution chloride 1 g. Te₂O₅ 100 ml. reaction of electrolysis 30 minutes. Voltage = 1 volt.

* Optimum condition + cf plate 7.

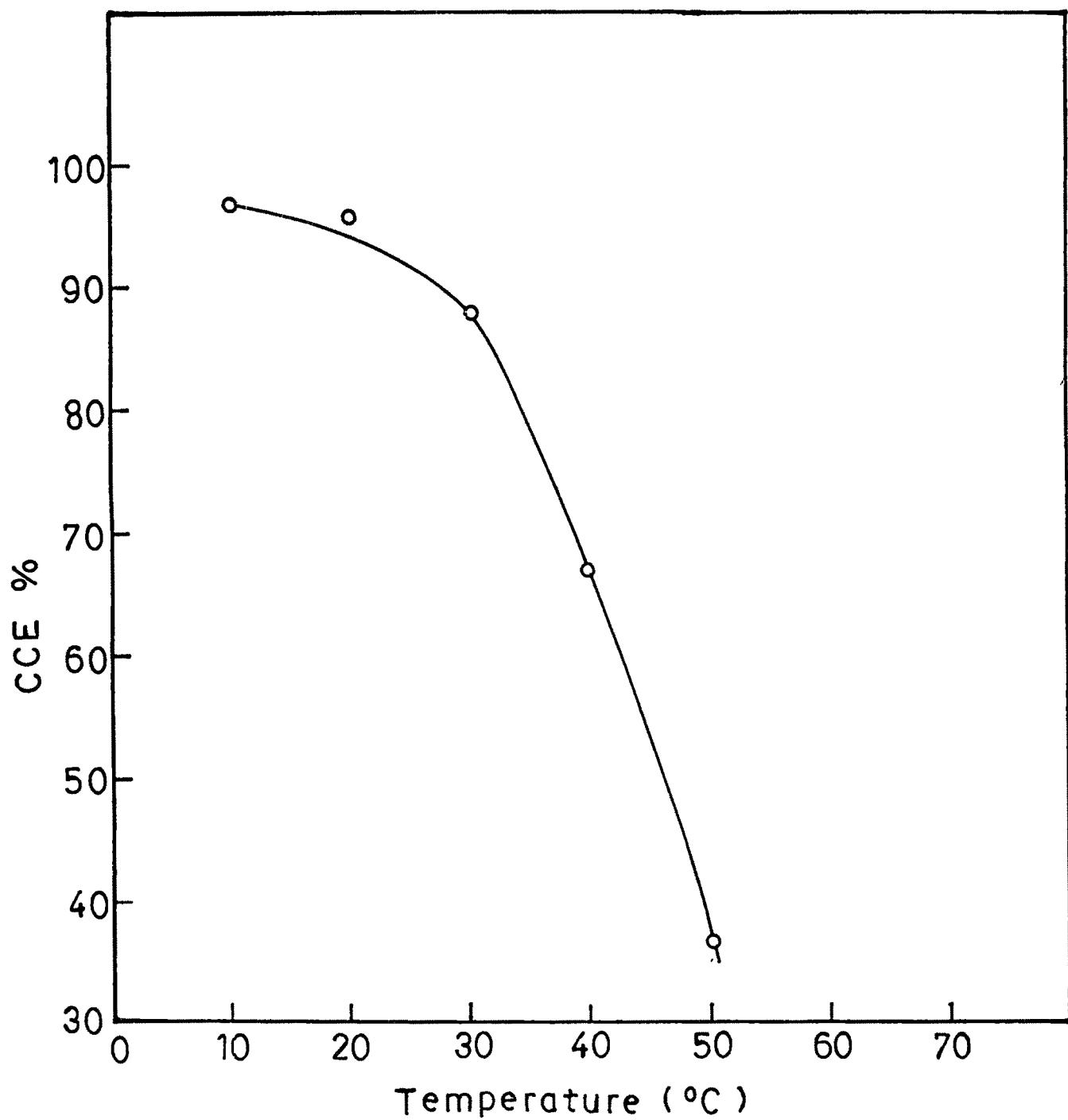


Fig. 13 – Effect of temperature on cathode current efficiency (CCE %) of Tin deposit .

* Optimum condition. + C.F. Plate 8.

Type formation tendency
measured.

50

60

70

80

90

100

110

120

130

140

150

160

170

180

190

200

210

220

230

240

250

260

270

280

290

300

310

320

330

340

350

360

370

380

390

400

410

420

430

440

450

460

470

480

0.005 36.24
0.006 36.91
0.007 38.65
0.008 39.35
0.009 40.05
0.010 40.75
0.011 41.45
0.012 42.15
0.013 42.85
0.014 43.55
0.015 44.25
0.016 44.95
0.017 45.65
0.018 46.35
0.019 47.05
0.020 47.75
0.021 48.45
0.022 49.15
0.023 49.85
0.024 50.55
0.025 51.25
0.026 51.95
0.027 52.65
0.028 53.35
0.029 54.05
0.030 54.75
0.031 55.45
0.032 56.15
0.033 56.85
0.034 57.55
0.035 58.25
0.036 58.95
0.037 59.65
0.038 60.35
0.039 61.05
0.040 61.75
0.041 62.45
0.042 63.15
0.043 63.85
0.044 64.55
0.045 65.25
0.046 65.95
0.047 66.65
0.048 67.35
0.049 68.05
0.050 68.75
0.051 69.45
0.052 70.15
0.053 70.85
0.054 71.55
0.055 72.25
0.056 72.95
0.057 73.65
0.058 74.35
0.059 75.05
0.060 75.75
0.061 76.45
0.062 77.15
0.063 77.85
0.064 78.55
0.065 79.25
0.066 79.95
0.067 80.65
0.068 81.35
0.069 82.05
0.070 82.75
0.071 83.45
0.072 84.15
0.073 84.85
0.074 85.55
0.075 86.25
0.076 86.95
0.077 87.65
0.078 88.35
0.079 89.05
0.080 89.75
0.081 90.45
0.082 91.15
0.083 91.85
0.084 92.55
0.085 93.25
0.086 93.95
0.087 94.65
0.088 95.35
0.089 96.05
0.090 96.75
0.091 97.45
0.092 98.15
0.093 98.85
0.094 99.55
0.095 100.25
0.096 100.95
0.097 101.65
0.098 102.35
0.099 103.05
0.100 103.75
0.101 104.45
0.102 105.15
0.103 105.85
0.104 106.55
0.105 107.25
0.106 107.95
0.107 108.65
0.108 109.35
0.109 110.05
0.110 110.75
0.111 111.45
0.112 112.15
0.113 112.85
0.114 113.55
0.115 114.25
0.116 114.95
0.117 115.65
0.118 116.35
0.119 117.05
0.120 117.75
0.121 118.45
0.122 119.15
0.123 119.85
0.124 120.55
0.125 121.25
0.126 121.95
0.127 122.65
0.128 123.35
0.129 124.05
0.130 124.75
0.131 125.45
0.132 126.15
0.133 126.85
0.134 127.55
0.135 128.25
0.136 128.95
0.137 129.65
0.138 130.35
0.139 131.05
0.140 131.75
0.141 132.45
0.142 133.15
0.143 133.85
0.144 134.55
0.145 135.25
0.146 135.95
0.147 136.65
0.148 137.35
0.149 138.05
0.150 138.75
0.151 139.45
0.152 140.15
0.153 140.85
0.154 141.55
0.155 142.25
0.156 142.95
0.157 143.65
0.158 144.35
0.159 145.05
0.160 145.75
0.161 146.45
0.162 147.15
0.163 147.85
0.164 148.55
0.165 149.25
0.166 149.95
0.167 150.65
0.168 151.35
0.169 152.05
0.170 152.75
0.171 153.45
0.172 154.15
0.173 154.85
0.174 155.55
0.175 156.25
0.176 156.95
0.177 157.65
0.178 158.35
0.179 159.05
0.180 159.75
0.181 160.45
0.182 161.15
0.183 161.85
0.184 162.55
0.185 163.25
0.186 163.95
0.187 164.65
0.188 165.35
0.189 166.05
0.190 166.75
0.191 167.45
0.192 168.15
0.193 168.85
0.194 169.55
0.195 170.25
0.196 170.95
0.197 171.65
0.198 172.35
0.199 173.05
0.200 173.75
0.201 174.45
0.202 175.15
0.203 175.85
0.204 176.55
0.205 177.25
0.206 177.95
0.207 178.65
0.208 179.35
0.209 179.85
0.210 180.55
0.211 181.25
0.212 181.95
0.213 182.65
0.214 183.35
0.215 183.85
0.216 184.55
0.217 185.25
0.218 185.95
0.219 186.65
0.220 187.35
0.221 187.85
0.222 188.55
0.223 189.25
0.224 189.85
0.225 190.55
0.226 191.25
0.227 191.95
0.228 192.65
0.229 193.35
0.230 193.85
0.231 194.55
0.232 195.25
0.233 195.85
0.234 196.55
0.235 197.25
0.236 197.85
0.237 198.55
0.238 199.25
0.239 199.85
0.240 200.55
0.241 201.25
0.242 201.95
0.243 202.65
0.244 203.35
0.245 203.85
0.246 204.55
0.247 205.25
0.248 205.85
0.249 206.55
0.250 207.25
0.251 207.85
0.252 208.55
0.253 209.25
0.254 209.85
0.255 210.55
0.256 211.25
0.257 211.95
0.258 212.65
0.259 213.35
0.260 213.85
0.261 214.55
0.262 215.25
0.263 215.85
0.264 216.55
0.265 217.25
0.266 217.85
0.267 218.55
0.268 219.25
0.269 219.85
0.270 220.55
0.271 221.25
0.272 221.95
0.273 222.65
0.274 223.35
0.275 223.85
0.276 224.55
0.277 225.25
0.278 225.85
0.279 226.55
0.280 227.25
0.281 227.85
0.282 228.55
0.283 229.25
0.284 229.85
0.285 230.55
0.286 231.25
0.287 231.95
0.288 232.65
0.289 233.35
0.290 233.85
0.291 234.55
0.292 235.25
0.293 235.85
0.294 236.55
0.295 237.25
0.296 237.85
0.297 238.55
0.298 239.25
0.299 239.85
0.300 240.55
0.301 241.25
0.302 241.95
0.303 242.65
0.304 243.35
0.305 243.85
0.306 244.55
0.307 245.25
0.308 245.85
0.309 246.55
0.310 247.25
0.311 247.85
0.312 248.55
0.313 249.25
0.314 249.85
0.315 250.55
0.316 251.25
0.317 251.95
0.318 252.65
0.319 253.35
0.320 253.85
0.321 254.55
0.322 255.25
0.323 255.85
0.324 256.55
0.325 257.25
0.326 257.85
0.327 258.55
0.328 259.25
0.329 259.85
0.330 260.55
0.331 261.25
0.332 261.95
0.333 262.65
0.334 263.35
0.335 263.85
0.336 264.55
0.337 265.25
0.338 265.85
0.339 266.55
0.340 267.25
0.341 267.85
0.342 268.55
0.343 269.25
0.344 269.85
0.345 270.55
0.346 271.25
0.347 271.95
0.348 272.65
0.349 273.35
0.350 273.85
0.351 274.55
0.352 275.25
0.353 275.85
0.354 276.55
0.355 277.25
0.356 277.85
0.357 278.55
0.358 279.25
0.359 279.85
0.360 280.55
0.361 281.25
0.362 281.95
0.363 282.65
0.364 283.35
0.365 283.85
0.366 284.55
0.367 285.25
0.368 285.85
0.369 286.55
0.370 287.25
0.371 287.85
0.372 288.55
0.373 289.25
0.374 289.85
0.375 290.55
0.376 291.25
0.377 291.95
0.378 292.65
0.379 293.35
0.380 293.85
0.381 294.55
0.382 295.25
0.383 295.85
0.384 296.55
0.385 297.25
0.386 297.85
0.387 298.55
0.388 299.25
0.389 299.85
0.390 300.55
0.391 301.25
0.392 301.95
0.393 302.65
0.394 303.35
0.395 303.85
0.396 304.55
0.397 305.25
0.398 305.85
0.399 306.55
0.400 307.25
0.401 307.85
0.402 308.55
0.403 309.25
0.404 309.85
0.405 310.55
0.406 311.25
0.407 311.95
0.408 312.65
0.409 313.35
0.410 313.85
0.411 314.55
0.412 315.25
0.413 315.85
0.414 316.55
0.415 317.25
0.416 317.85
0.417 318.55
0.418 319.25
0.419 319.85
0.420 320.55
0.421 321.25
0.422 321.95
0.423 322.65
0.424 323.35
0.425 323.85
0.426 324.55
0.427 325.25
0.428 325.85
0.429 326.55
0.430 327.25
0.431 327.85
0.432 328.55
0.433 329.25
0.434 329.85
0.435 330.55
0.436 331.25
0.437 331.95
0.438 332.65
0.439 333.35
0.440 333.85
0.441 334.55
0.442 335.25
0.443 335.85
0.444 336.55
0.445 337.25
0.446 337.85
0.447 338.55
0.448 339.25
0.449 339.85
0.450 340.55
0.451 341.25
0.452 341.95
0.453 342.65
0.454 343.35
0.455 343.85
0.456 344.55
0.457 345.25
0.458 345.85
0.459 346.55
0.460 347.25
0.461 347.85
0.462 348.55
0.463 349.25
0.464 349.85
0.465 350.55
0.466 351.25
0.467 351.95
0.468 352.65
0.469 353.35
0.470 353.85
0.471 354.55
0.472 355.25
0.473 355.85
0.474 356.55
0.475 357.25
0.476 357.85
0.477 358.55
0.478 359.25
0.479 359.85
0.480 360.55
0.481 361.25
0.482 361.95
0.483 362.65
0.484 363.35
0.485 363.85
0.486 364.55
0.487 365.25
0.488 365.85
0.489 366.55
0.490 367.25
0.491 367.85
0.492 368.55
0.493 369.25
0.494 369.85
0.495 370.55
0.496 371.25
0.497 371.95
0.498 372.65
0.499 373.35
0.500 373.85
0.501 374.55
0.502 375.25
0.503 375.85
0.504 376.55
0.505 377.25
0.506 377.85
0.507 378.55
0.508 379.25
0.509 379.85
0.510 380.55
0.511 381.25
0.512 381.95
0.513 382.65
0.514 383.35
0.515 383.85
0.516 384.55
0.517 385.25
0.518 385.85
0.519 386.55
0.520 387.25
0.521 387.85
0.522 388.55
0.523 389.25
0.524 389.85
0.525 390.55
0.526 391.25
0.527 391.95
0.528 392.65
0.529 393.35
0.530 393.85
0.531 394.55
0.532 395.25
0.533 395.85
0.534 396.55
0.535 397.25
0.536 397.85
0.537 398.55
0.538 399.25
0.539 399.85
0.540 400.55
0.541 401.25
0.542 401.95
0.543 402.65
0.544 403.35
0.545 403.85
0.546 404.55
0.547 405.25
0.548 405.85
0.549 406.55
0.550 407.25
0.551 407.85
0.552 408.55
0.553 409.25
0.554 409.85
0.555 410.55
0.556 411.25
0.557 411.95
0.558 412.65
0.559 413.35
0.560 413.85
0.561 414.55
0.562 415.25
0.563 415.85
0.564 416.55
0.565 417.25
0.566 417.85
0.567 418.55
0.568 419.25
0.569 419.85
0.570 420.55
0.571 421.25
0.572 421.95
0.573 422.65
0.574 423.35
0.575 423.85
0.576 424.55
0.577 425.25
0.578 425.85
0.579 426.55
0.580 427.25
0.581 427.85
0.582 428.55
0.583 429.25
0.584 429.85
0.585 430.55
0.586 431.25
0.587 431.95
0.588 432.65
0.589 433.35
0.590 433.85
0.591 434.55
0.592 435.25
0.593 435.85
0.594 436.55
0.595 437.25
0.596 437.85
0.597 438.55
0.598 439.25
0.599 439.85
0.600 440.55
0.601 441.25
0.602 441.95
0.603 442.65
0.604 443.35
0.605 443.85
0.606 444.55
0.607 445.25
0.608 445.85
0.609 446.55
0.610 447.25
0.611 447.85
0.612 448.55
0.613 449.25
0.614 449.85
0.615 450.55
0.616 451.25
0.617 451.95
0.618 452.65
0.619 453.35
0.620 453.85
0.621 454.55
0.622 455.25
0.623 455.85
0.624 456.55
0.625 457.25
0.626 457.85
0.627 458.55
0.628 459.25
0.629 459.85
0.630 460.55
0.631 461.25
0.632 461.95
0.633 462.65
0.634 463.35
0.635 463.85
0.636 464.55
0.637 465.25
0.638 465.85
0.639 466.55
0.640 467.25
0.641 467.85
0.642 468.55
0.643 469.25
0.644 469.85
0.645 470.55
0.646 471.25
0.647 471.95
0.648 472.65
0.649 473.35
0.650 473.85
0.651 474.55
0.652 475.25
0.653 475.85
0.654 476.55
0.655 477.25
0.656 477.85
0.657 478.55
0.658 479.25
0.659 479.85
0

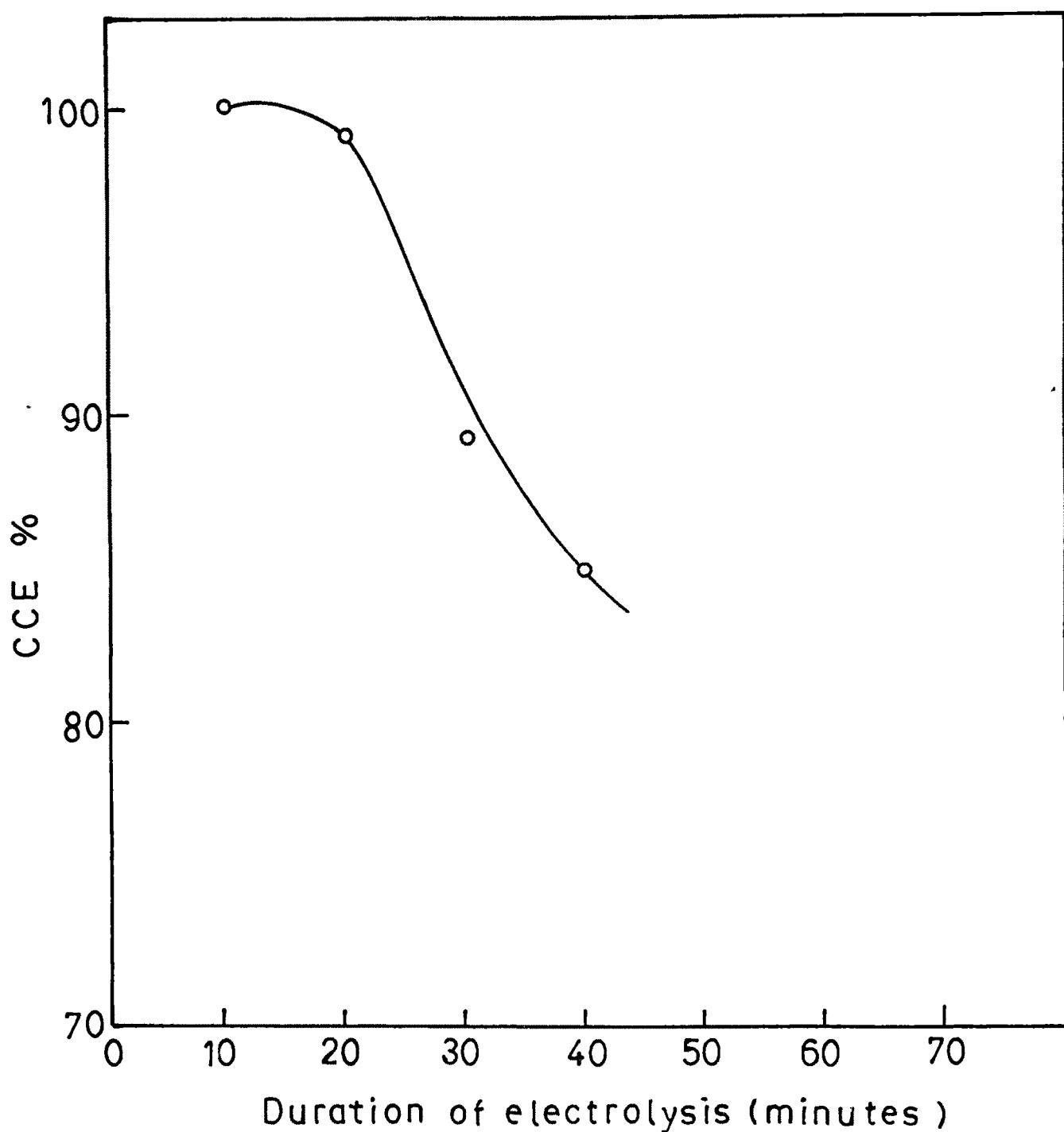


Fig. 14 —Effect of duration of electrolysis on cathode current efficiency (CCE %) of Tin deposit .

+ cf. plate g.

TABLE NO. 15 - The effect of electrode distance on the metal content and the percentage of soluble current efficiency (see Fig. 1) of the deposit.

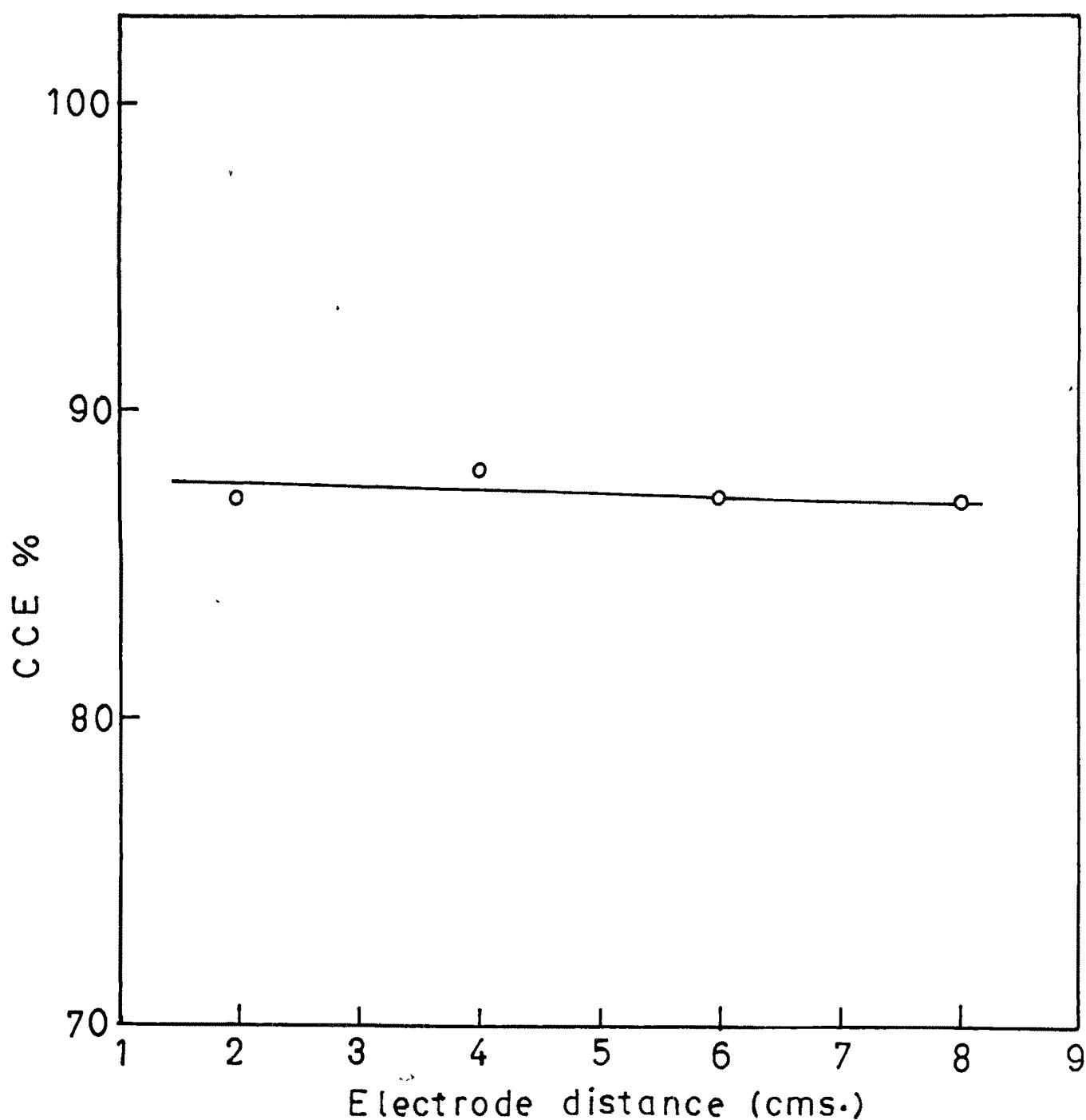


Fig. 15 – Effect of electrode distance on cathode current efficiency (CCE %) of Tin deposit.

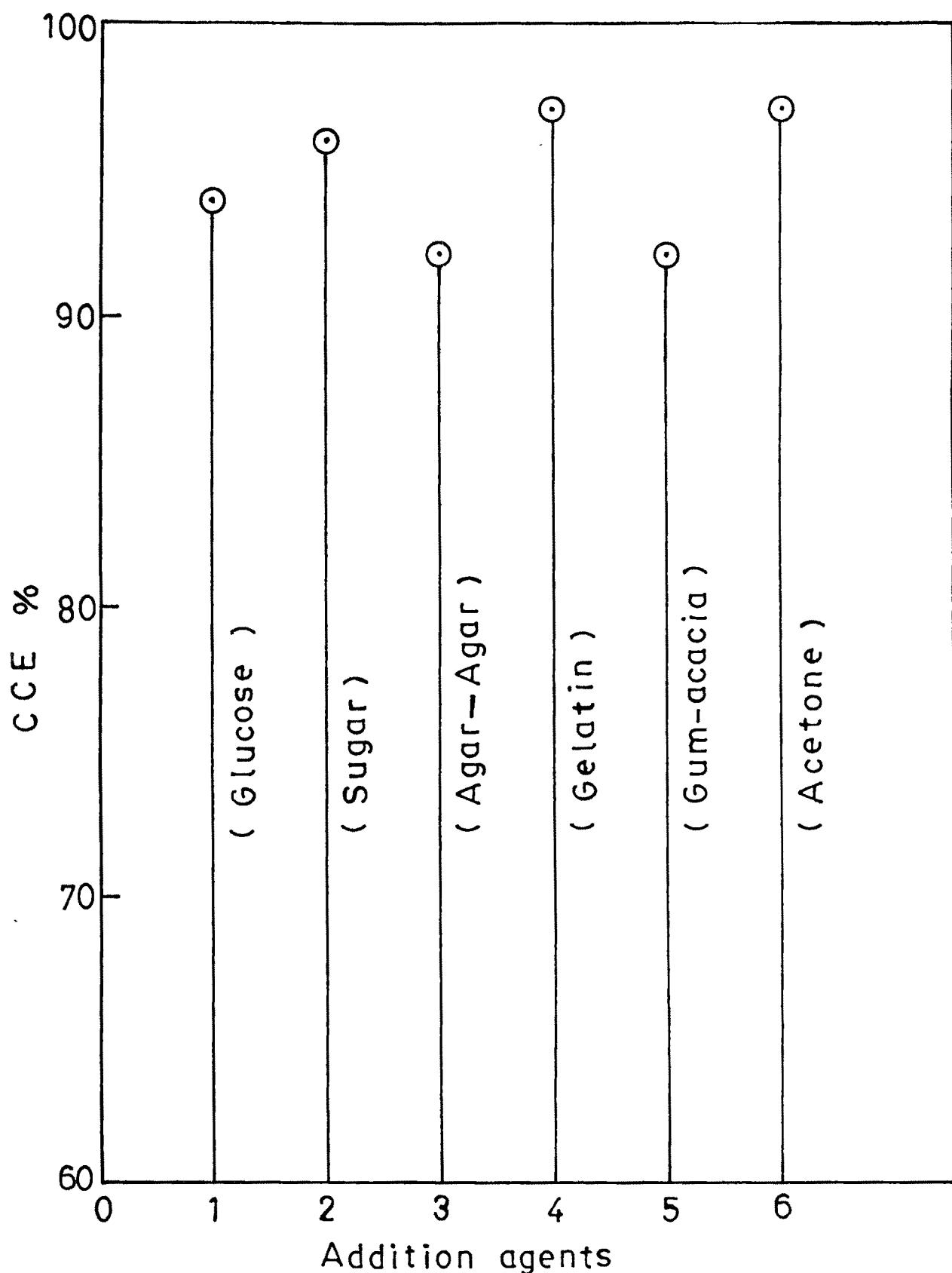
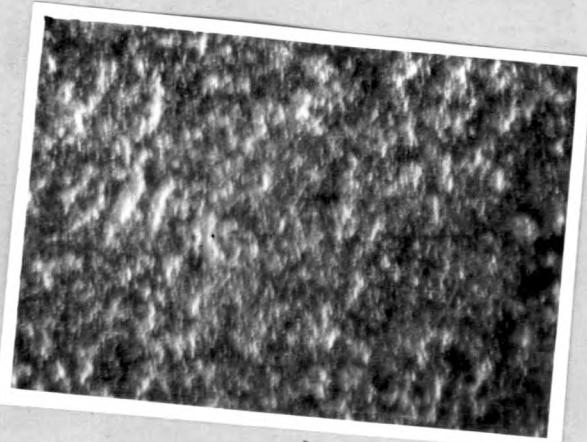


Fig. 16—Effect of addition agents on cathode current efficiency (CCE %) of Tin deposit .

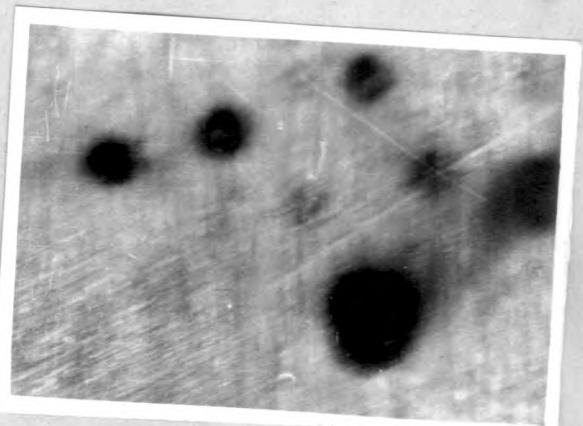
SUMMARYTIN SYSTEM (OPTIMUM CONDITIONS)

Table 16-4 : 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 summarised below:

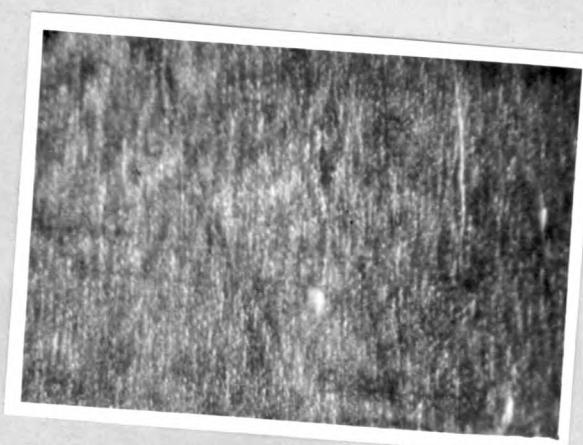
| Parameter studied and Range | Optimum condition |
|--|--------------------------------------|
| 1) Composition of the bath | - |
| a)Concn. of tin chloride 2-8 gms. per 100 ml of the solution. | 4 gms per 100 ml of the solution. |
| b)Concn. of hydrochloric acid -0.4 to 1.0 Normal (Normality in mixture). | 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 - 0.064 -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. |



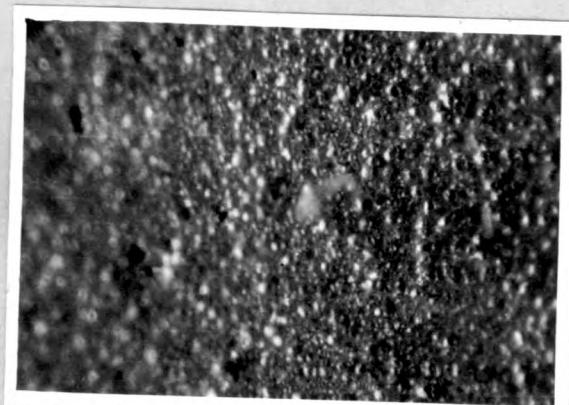
6



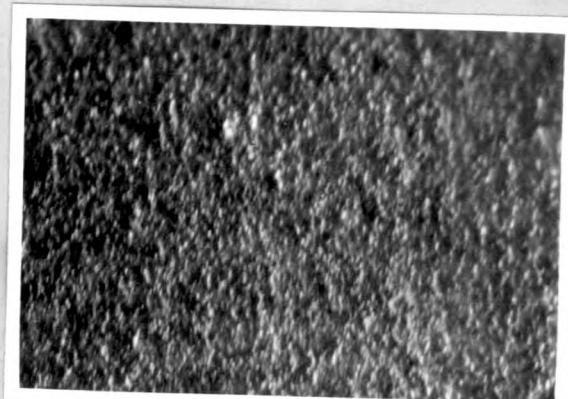
7



8



9



10

cf. plate 6-10 (Tin)

MARR. BALASAHEB KHARDEKAR LIBRARY
SHIVAJI UNIVERSITY, KOLHAPUR

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 8 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, truing effect was observed, but as concentration was increased, no truing 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 ampero-hour in the cold 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 C.C. observed was above 95 % in general. From Table - 10, it was observed that, at 0.0 M 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 - 11.1.

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 lustrious, 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 30% 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 - 1.06 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 S.T. tin content and %S of the deposit were increased to a great extent.

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

The temperature range studied was 10° - 50° C, under optimum conditions of bath composition and C.R. The tin content in the deposit decreased with increase in temperature. The quality of the deposits was found to be satisfactory at 20° 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 (as 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 G.S decreased steadily. The deposits were bright uniform, and adherent 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 (as Table -15, Fig.15) :

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

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

A number of addition agents were added separately and singly to the bath under optimum conditions and the results are summarized 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 while 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 Sn and Zn deposition. The deposition of metals, according to Ullman¹, 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 nuclei 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.

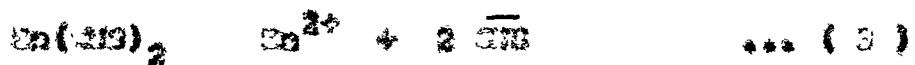
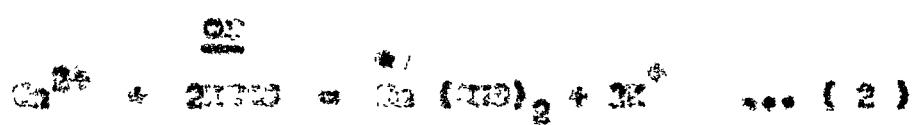
Composition of the bath has marked effects on the relative velocities of nuclei formation and on their subsequent crystal growth. The cathode polarization and the structure of the deposit also play their own role. It would appear that for the production of a rapid and thick deposit, the presence of a 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 hasty, spongy deposits results. Agitation of the solution would bring the other metal

ions nearer to the cathode but at the same time it strips the sludge that is invariably found at the bottom of the bath. This precipitate settles 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 ionizes in two or more stages, the metal usually being ionized 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 thiocyanate 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 $Zn(OH)_2$ or $Zn(OH)_3$, and others hitherto unknown, might get formed. Thio-cyanide ions are bound up with zinc. We have however $\stackrel{\text{no}}{\Rightarrow}$ specific evidence for the formation of different types of complexes to attain equilibrium. As such we have to depend on the scarce data available with us indicating the formation of the following types of complexes with known instability constants γ and for overall complex and the others for stepwise dissociation complexes.

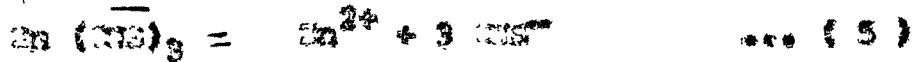
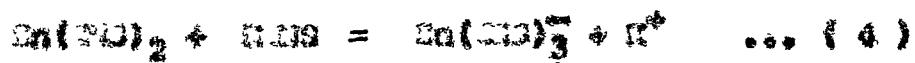
The high sulphocyanide concentrations gives maximum conductivity and also provides largely as a complexing ion in stabilizing $\text{Sn}(\text{SCN})_2^*$, forming complex salts of probable compositions. The most important variables in controlling the formation of specific complexes are the pH and the thiocyanate content of the bath. The complexes of the types mentioned may be supposed to dissociate as follows :

Sn-complexes (thiocyanate bath) :

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



* Equilibrium or Dissociation constant being not very low (about 10^{-30}) may yield a complex $\text{Sn}(\text{SCN})_3$ as follows :



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



The further growth of deposit follows the law of adsorption.

Dense parts of the anode are deposited by fresh metal ions for their turn to be discharged.

Tin Complexes (Acid Chloride Path) :

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

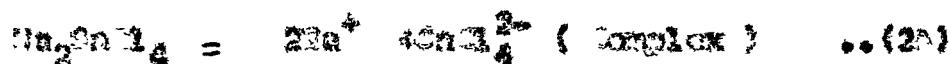
Stannous and Stannic Complexes :



OR



OR



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



Alternatively, as the bath edges and the stannous tin oxides, 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.

