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APPLICATION OF VOLTAMMETRY TO COPPER ELECTRODEPOSITION

by

LOUIS FRANCIS TOTH, JR., 1947-

A DISSERTATION

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Finally, the author expresses his graditude to Mr. Harlan W. Rice for his assistance with the scanning electron microscope.

ABSTRACT

A study was undertaken to determine the feasibility of using voltammetry and scanning electron microscopy techniques to characterize copper deposition from an acid-sulfate electrolyte. The main process variables investigated were temperature and addition agents (chloride ion, glue, separan or thiourea) at different concentrations, over a range of current densities. Cathodes employed were either polycrystalline titanium or copper. Some long-time copper deposits were also made using Ti cathodes and the orientations of these deposits were determined by x-ray diffraction.

Observations of copper crystals produced during voltammetry scans, on a Ti cathode, indicated that a characteristic morphology was associated with each type of addition agent. Temperature also affected the physical appearance of the deposited copper. With a Cu cathode the crystal morphologies were essentially identical, regardless of the addition agent used. At a constant scanning rate of 1 mV/sec, the various addition agents, on both Ti and Cu cathodes, gave characteristic and reproducible voltammograms. Shifts and relative differences between the polarization curves were also noted with changing temperature.

The results of this investigation indicate that there is a definite correlation between type and concentration of addition agent and voltammogram. The substrate used in the deposition process also has an effect. A definite relationship exists between the morphology of the copper and the processing conditions used during deposition. It thus seems that a combination of voltammetry and scanning electron microscopy would be potentially useful in predicting the electrolyzability of commercial copper refining or winning solutions.

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I. INTRODUCTION

A major problem encountered in commercial electrodeposition of copper is control of the physical nature and morphology of the deposit. There are numerous control methods available and used to insure production of optimum quality deposits. However, these methods sometimes give mixed or limited success and many times it is a matter of trial and error in correcting a system that is producing an unsatisfactory product. Frequently, the possible corrective action is undesirable from the standpoint that it would adversely affect production rates and efficiencies. The problem is often cyclic in nature, with periods of wide variation in the type of deposit obtained, but without any apparent chemical or physical change in process.

A wide variety of addition agents is often added, in rather small concentrations, for enhancement of deposit quality. This makes characterization of the electrolyte chemistry quite difficult or sometimes even impossible. The ultimate test then is cell room performance and this can prove to be an expensive means of deposit evaluation. Therefore, because of a very critical dependence of the electrochemical aspects of the process on trace impurities or slight variations in electrolyte composition, it would be desirable to develop a method whereby a determination could be made as to the controlling factors in the cathodic electrodeposition process.

Considerable research has been done to delineate the exact mechanisms by which addition agents function during deposition. Still, little is known as to the electrochemical activity and behavior of the various additives. Studies [1-12,16] dealing with the effects of anions and organics on the current-potential relationships and morphology of the copper deposits have also been made. The electrochemical activity of these additions has been correlated to polarization effects and changes in the kinetics of the deposition process. In these various studies potentiostatic or galvanostatic techniques coupled with x-ray and microscopy were used. Also, radioactive labeling [8] was employed to investigate the cathodic adsorption of the additions. More recently a potentiostatic scan method [7] was used to study the addition agent's function in solution. One conclusion was that a disruption in the diffusion layer occurred during deposition.

The objective of this work was to investigate the feasibility of combining voltammetry and scanning electron microscopy to develop a technique for electrolyte characterization and control. It was hoped that this technique would allow the electroactive species in the deposition process to be elucidated. This cannot normally be accomplished by standard analysis due to the synergistic effects of the various electrolyte components. Ultimately, this technique would also provide some insight into the actual mechanics of the deposition process.

In addition to the short time scans, long time deposits could prove useful as a basis for comparison of the end result of the deposition process. Changes in the overall growth mode and crystal habit of the electrodeposits with time could also be determined.

Copper and titanium were chosen as cathode materials in this investiation because they are the most common substrates presently in use.

II. EXPERIMENTAL

A Wenking model 70HP10 potentiostat was used in conjunction with a Wenking model VSG72 voltage scan generator which allowed the desired conditons (scan rate, scan range, start potential, etc.) to be applied automatically. The voltammograms generated were recorded on a Moseley 135Am X-Y recorder. A Keithley 610C electrometer was used to measure potentials. Figure 1 is a schematic diagram of the apparatus. The experiments were conducted in a pyrex "H" cell in a constant temperature water bath. The cathodes were either copper or titanium prepared from high purity rod stock. The exposed surface area of the copper cathode was 1.26 cm^2 and that of the titanium was 0.5 cm^2. The anode was constructed from an electrodeposited copper sheet. The reference electrode was Hg/Hg_2SO_4 (1M H_2SO_4).

Both types of cathodes were prepared for each experimental run by wet grinding on 240 to 600 grit Carbimet paper. The electrodes were then washed with acetone in an ultrasonic cleaner, rinsed with acetone and dried in an air stream, and immediately placed in the "H" cell. Electrolyte, 300 ml, of the proper composition, was introduced into the cell, the anode was placed into the proper compartment, and the reference electrode attached before placing the completed assembly into the

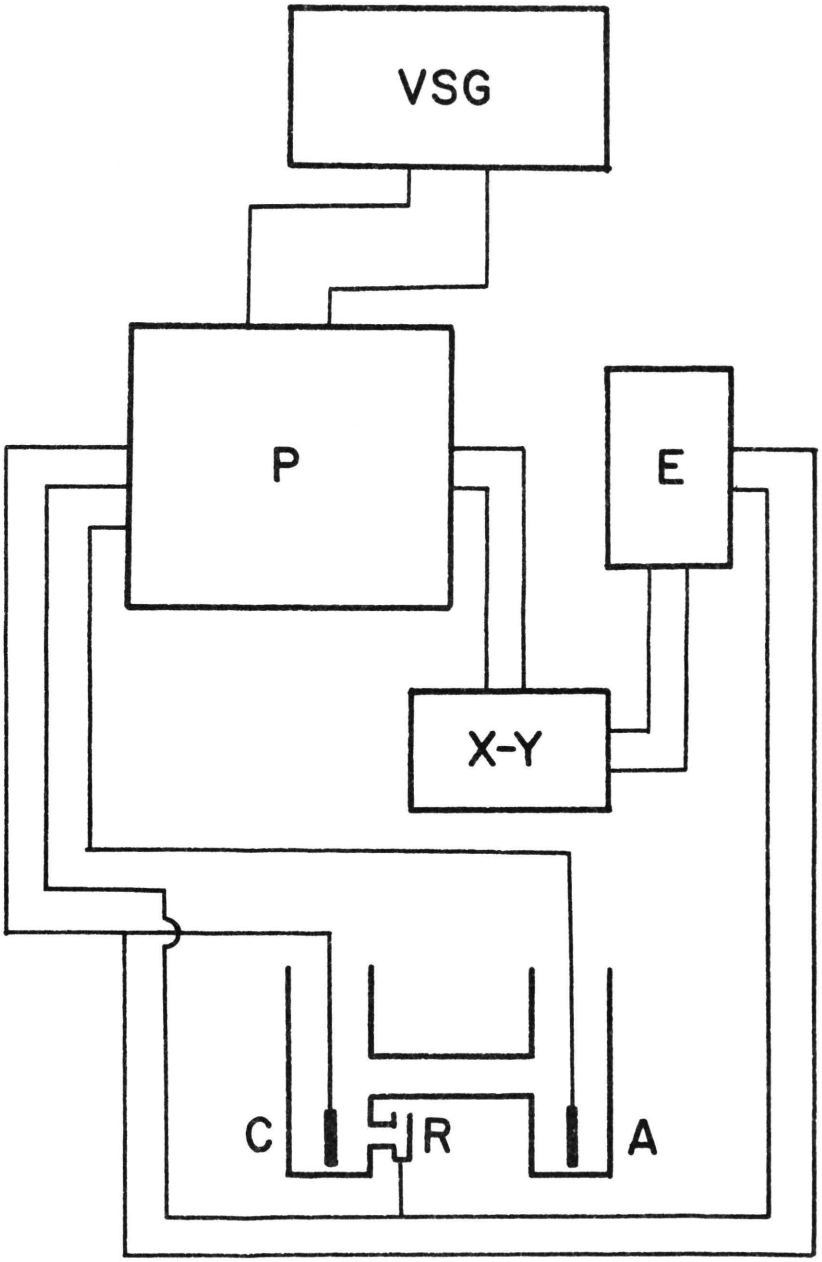

Figure 1. SCHEMATIC FOR APPARATUS SET-UP. VSG = VOLTAGE SCAN GENERATOR; P = POTENTIOSTAT; E = ELECTROMETER; X-Y = X-Y RECORDER; C = CATHODE; R = REFERENCE ELECTRODE (MERCUROUS SULFATE); A = ANODE.

water bath. A flow of prepurified nitrogen through the cell was then begun and continued throughout the experimental run. The cell was allowed to equilibrate for 15 minutes before each experiment. With a copper cathode, the voltammograms were begun at the rest potential, which was approximately +0.285 volts (SHE). With the titanium cathode the voltammograms were begun at +0.325 volts (SHE). The complete voltage scan was made at a rate of 1.0 mV/ sec.

When it was desired to examine the copper electrodeposits by the SEM, a slightly different procedure was used. Attempts were made to produce the copper deposits on an approximately equal current basis. The scan generator was engaged and scanned cathodically to a current density of 40 ma/cm^2, then reversed and scanned in an anodic direction to a current density of 16 ma/cm^2. The electrode was held at whatever overpotential was necessary to maintain the latter current density for 60 seconds. The electrode was immediately removed from the cell, washed with distilled water, rinsed with acetone and dried in an air stream. The entire procedure was performed as rapidly as possible to prevent oxidation of the copper electrodeposit before examination.

The electrolyte was prepared from Fisher A300C sulfuric acid and copper sulfate pentahydrate. These two components were mixed with distilled water to obtain a concentration of 45 gpl Cu^{++} and 200 gpl H_2SO_4. The copper concentration was determined by iodine-thiosulfate-starch titration, while the acid concentration was determined by titration with Fisher 1N sodium hydroxide standard solution. Before each experimental run the electrolyte concentration was checked and adjusted, if necessary.

Copper was also galvanostatically deposited on titanium cathodes at times between 12 and 48 hours depending on current density. These deposits were made to provide a basis for comparison with the copper electrodeposits produced by voltammetry. The orientations of these galvanostatic deposits were determined by x-ray diffraction, and scanning electron microscopy was used to examine the surface morphology.

III. VOLTAMMETRY EXPERIMENTS

A. Copper Cathode

1. Unadulterated Electrolyte. Experimentation was performed on the copper cathode using the unadulterated electrolyte (no additives in the solution), at temperatures of 30, 40, 50 and 60°C. The voltammograms were cycled forward (cathodically) from rest potential, to -200 mV overpotential, then back (anodically) to the original rest potential. The effect of temperature on the voltammograms is shown in Figure 2. These unadulterated electrolyte scan curves were used as a basis for comparison with the voltammograms generated from electrolytes to which various addition agents had been added.

2. Chloride Ion Additions. Solutions containing chloride ion, added as HCl, produced a voltammogram of the type shown in Figure 3. These voltammograms showed more polarization (lower currents) than those for the unadulterated solutions. Increasing the chloride ion content, under isothermal conditons, resulted in a slight increase of the overall current. Also, the magnitude of the current generated during either the cathodic and anodic sweep was very similar. Increasing the electrolyte temperature, at constant chloride ion content, depolarized

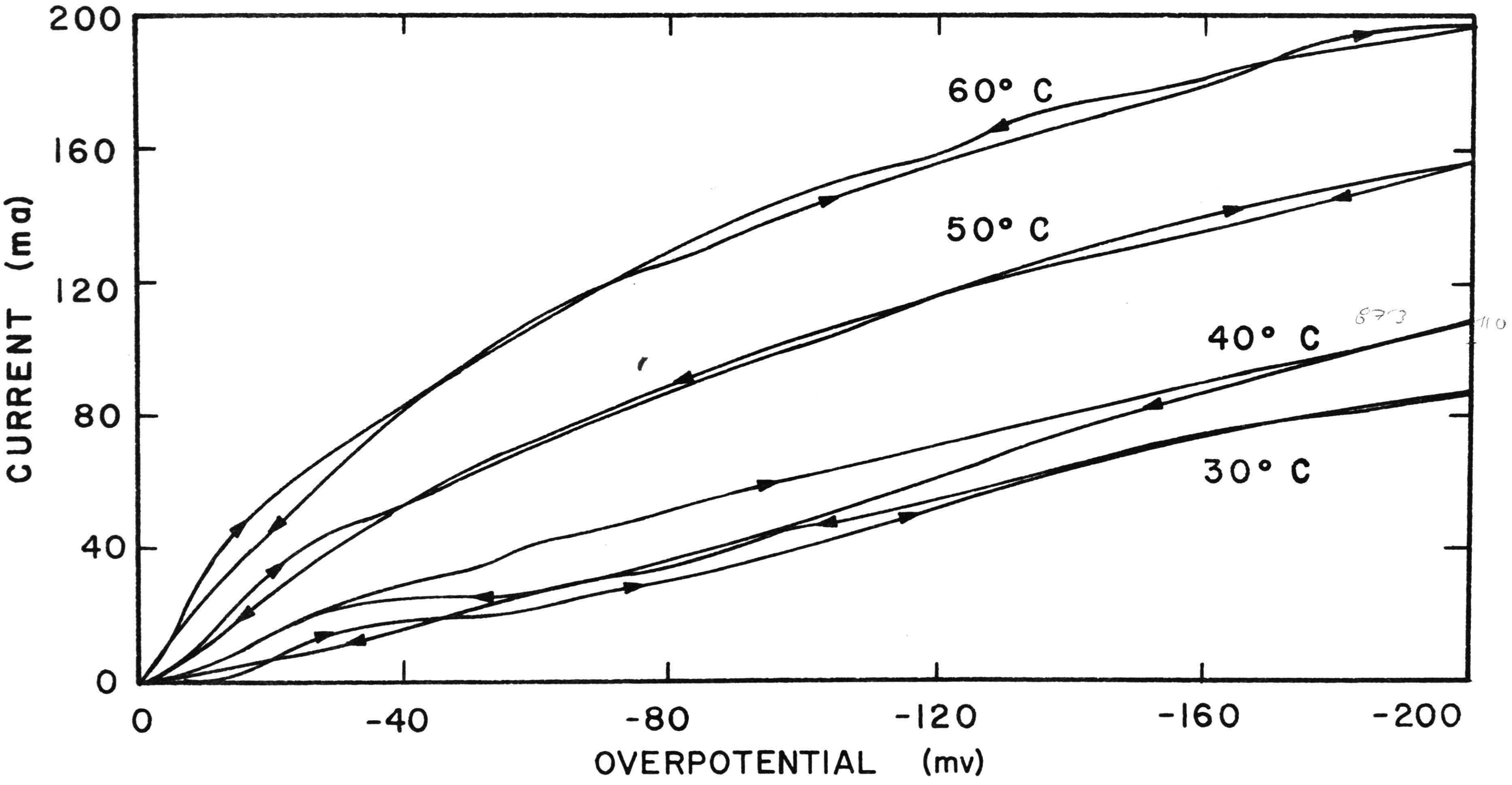

Figure 2. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30, 40, 50 and 60°C. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

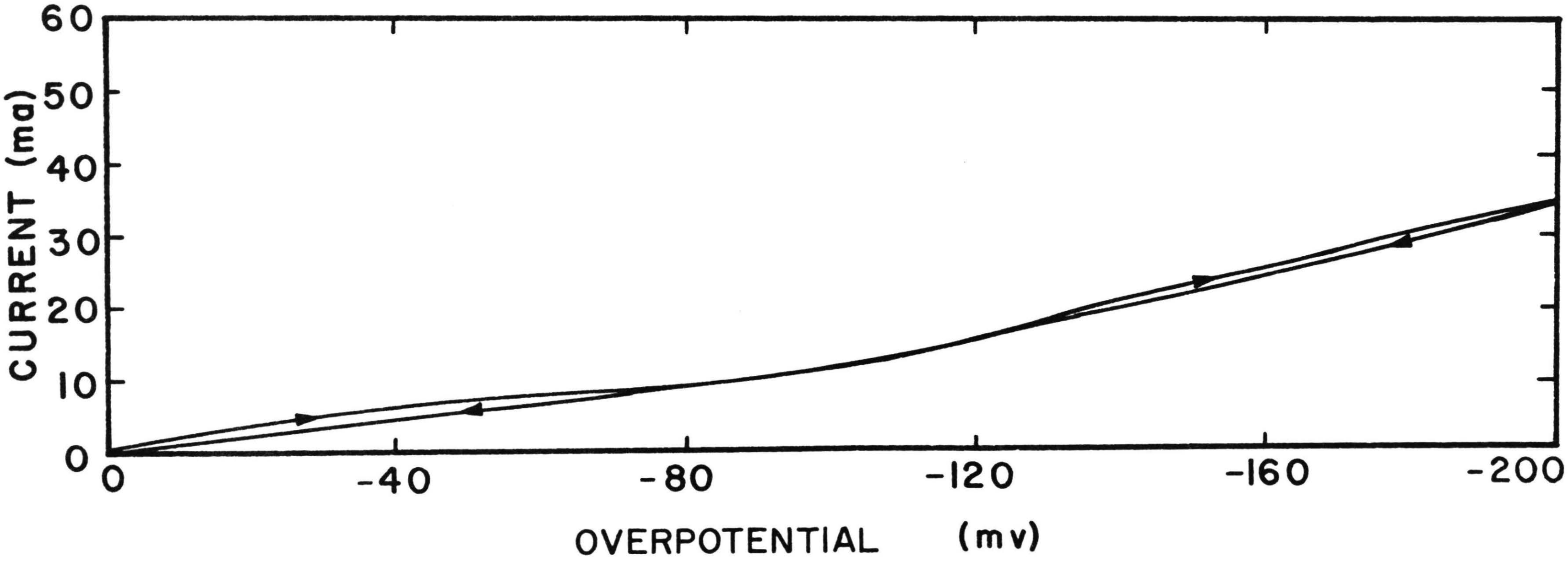

Figure 3. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30°C CONTAINING 10 mg/l CHLORIDE ION. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

the deposition process similar to the unadulterated electrolyte.

3. Glue and Separan Additions. Typical voltammograms from glue-or separan-containing electrolytes are illustrated in Figures 4 and 5. These voltammograms resemble the unadulterated electrolyte voltammograms except that the initial current plateau was shifted in a more cathodic direction. The anodic sweeps were also always more polarized than the cathodic sweeps. Increases in the additive content, under isothermal conditions further polarized the deposition process. Increasing the electrolyte temperature, at constant additive concentration, resulted in an increase in the magnitude of the plateau current. A shift of the initiation of the current plateau to more anodic overpotentials and a decrease in the breadth of the current plateau also occurred.

4. Thiourea Additions. The thiourea-containing solutions produced voltammograms exhibiting striking differences in appearance. Relative changes in the scan curves with temperature and additive concentration variations were also more pronounced. Voltammograms obtained from solutions containing 10 mg/l thiourea showed a current peak on the cathodic sweep at approximately +0.190 volts (SHE) and typical scans at 40 and

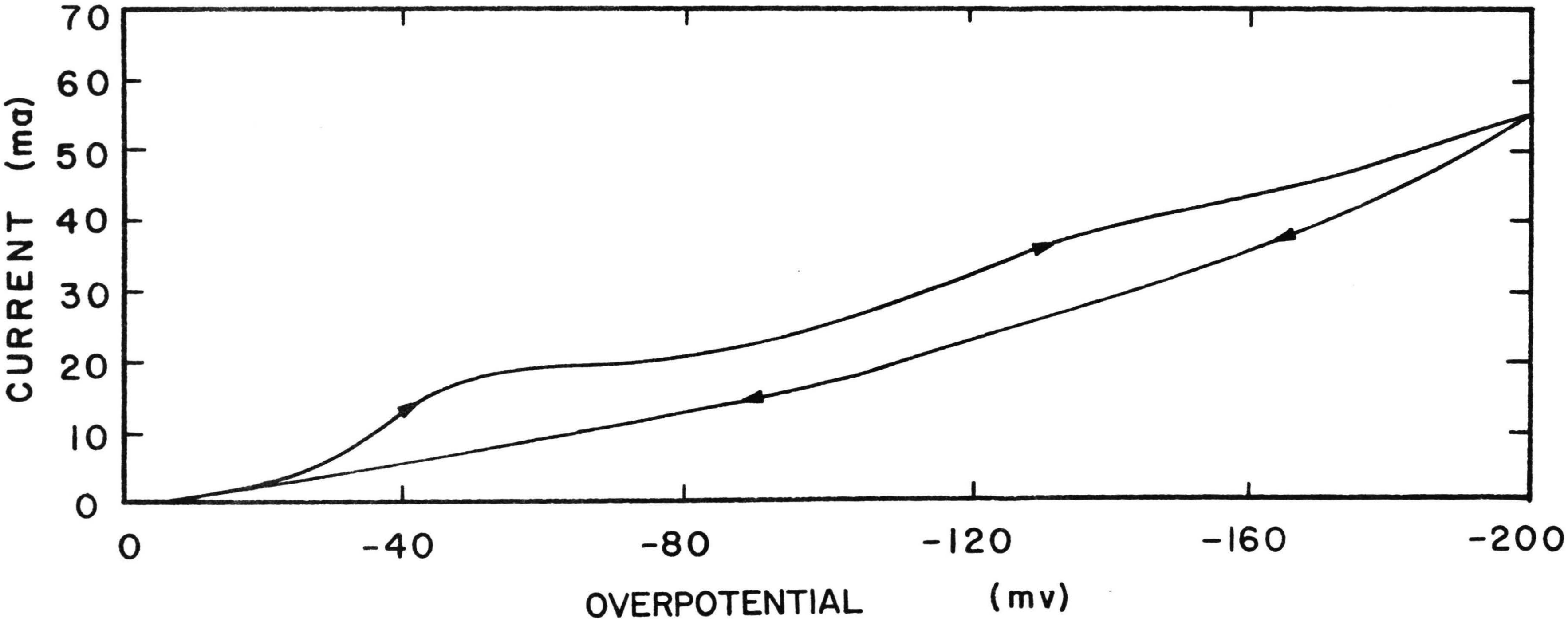

FIGURE 4. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30°C CONTAINING 10 mg/l GLUE. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

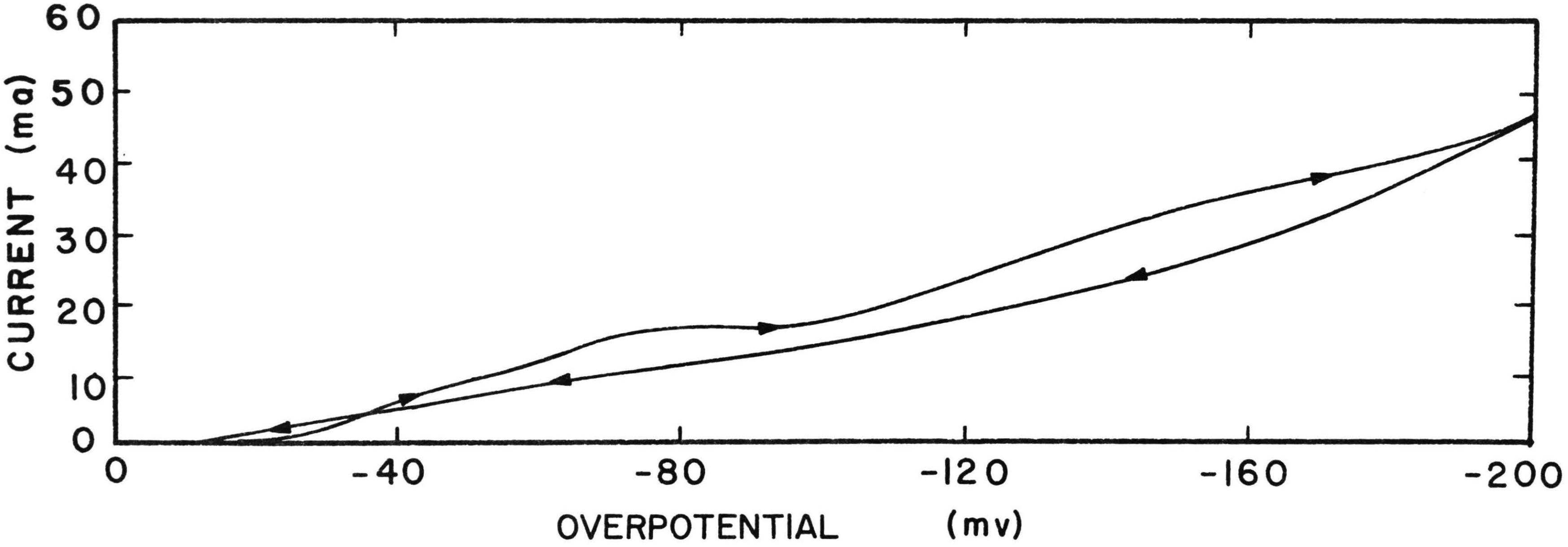

FIGURE 5. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30°C CONTAINING 50 mg/l SEPARAN (DOW NP-10). AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

50°C are shown in Figures 6 and 7. These characteristic peaks produced higher currents than the unadulterated cathodic sweeps at the same values of overpotential. At 50 and 60°C, a current peak was also noted on the anodic sweep but the peak was shifted in a slightly more anodic direction. These current peaks were indicative of another reaction taking place during the metal deposition process. When the thiourea concentration was increased above 25 mg/l, a voltammogram of the type shown in Figure 8 resulted. The cathodic sweep shows an extensive current plateau which persists to approximately -300 mV overpotential. This type of current plateau would be expected if adsorption or cathodic film formation occurred. The anodic sweeps produced higher currents than the cathodic ones; and a small current peak was also produced on some of the anodic sweeps. Furthermore, slight variations, such as a curvature imparted to some of the cathodic sweeps, were noted at higher concentrations and temperatures.

Increasing the electrolyte temperature with solutions containing 10 mg/l thiourea, increased the maximum current produced by the reaction peak. At thiourea concentrations above 25 mg/l the plateau current also increased. At a constant temperature, increasing the electrolyte thiourea concentration increased polarization.

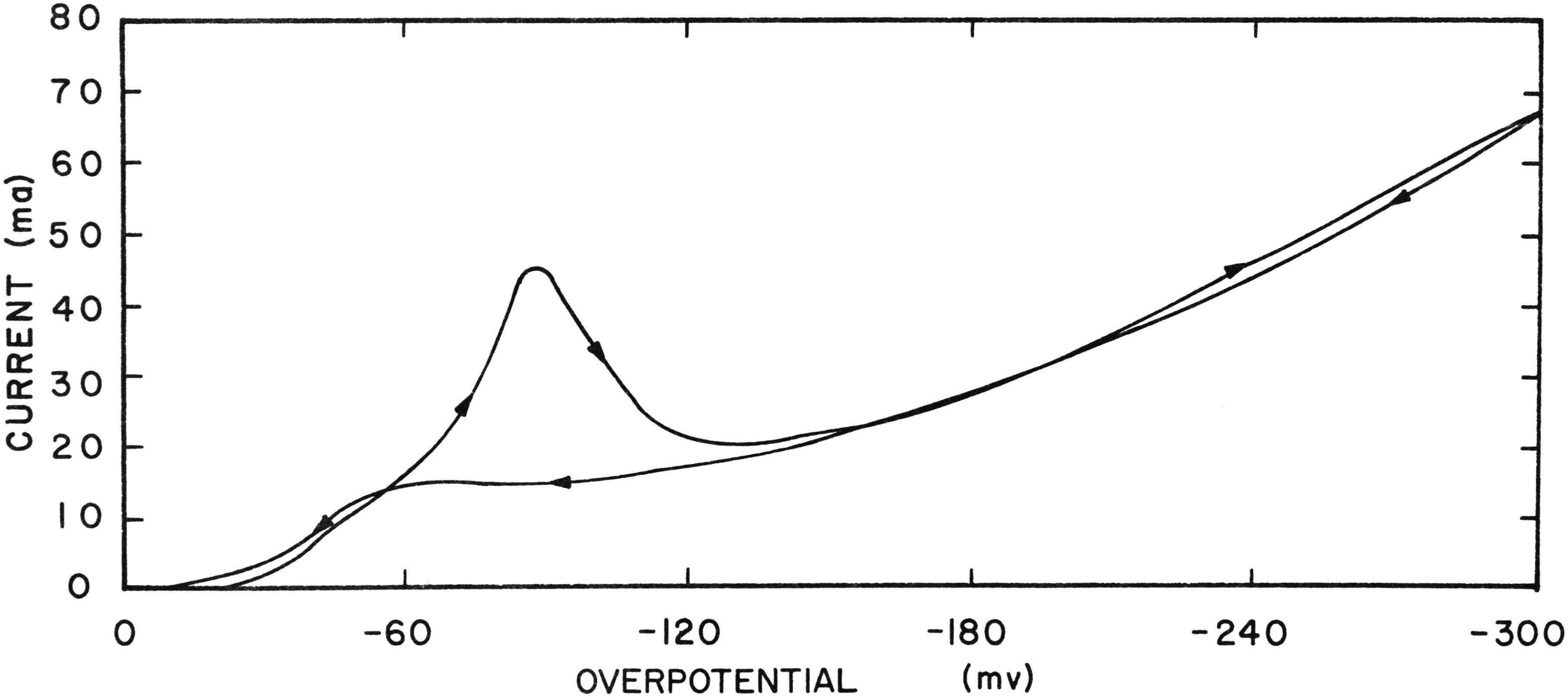

FIGURE 6. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 10 mg/l THIOUREA. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

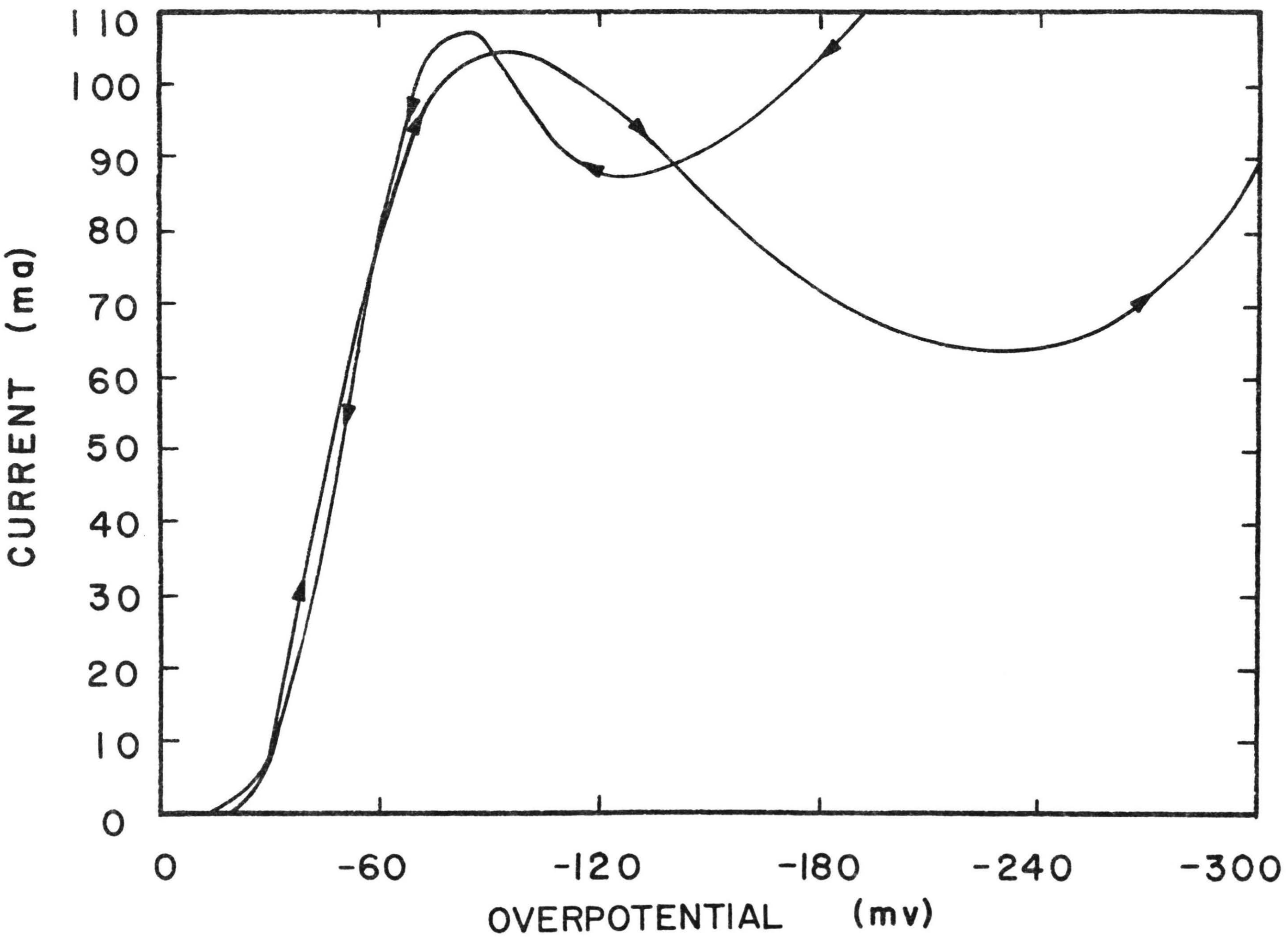

FIGURE 7. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 50°C CONTAINING 10 mg/l THIOUREA. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

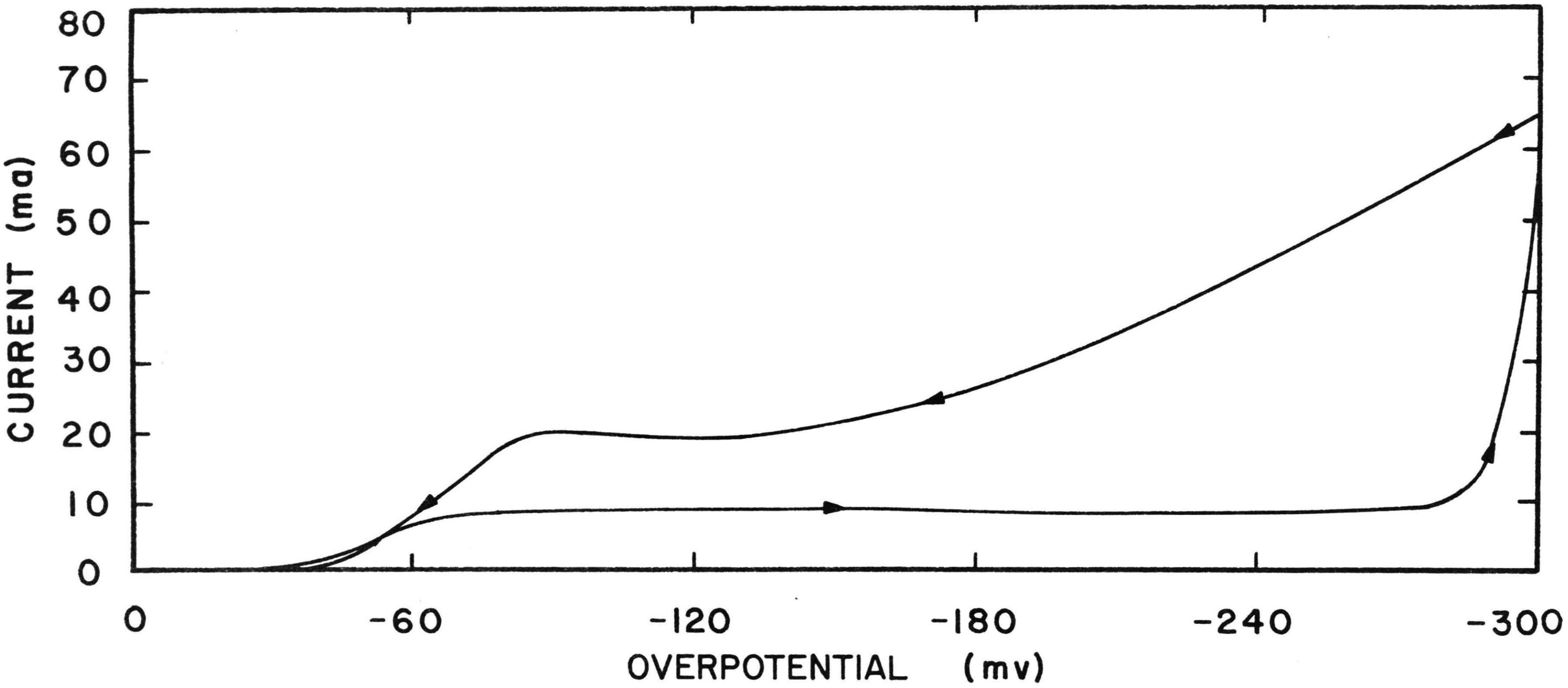

FIGURE 8. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30°C CONTAINING 50 mg/l THIOUREA. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

B. Titanium Cathode

Voltammograms were also generated using a Ti substrate but the relative changes and effects of the additives on the scan curves were much less dramatic then similar ones on a Cu substrate. Some characteristics were noted but they were considerably less definitive than those shown previously.

1. Unadulterated Electrolyte.

Voltammograms were generated with this electrolyte from an initial potential of +0.325 volts (SHE). The potential was scanned cathodically to an overpotential of -300 mV, reversed and anodically scanned back to the original starting potential. The voltammograms at the four temperatures are shown in Figure 9. These indicate that increasing the electrolyte temperature depolarizes the deposition process. Also, the anodic sweeps always produce higher currents than the cathodic sweeps.

2. Chloride Ion, Glue and Separan Additions.

Illustrated in Figures 10, 11 and 12 are the voltammograms typical of those produced with chloride ion-, glue or-separan-containing solutions. The shapes of the voltammograms were generally similar, except for minor variations occurring in the cathodic sweep portions. These parts of the curve were also always more polarized than the anodic sweeps.

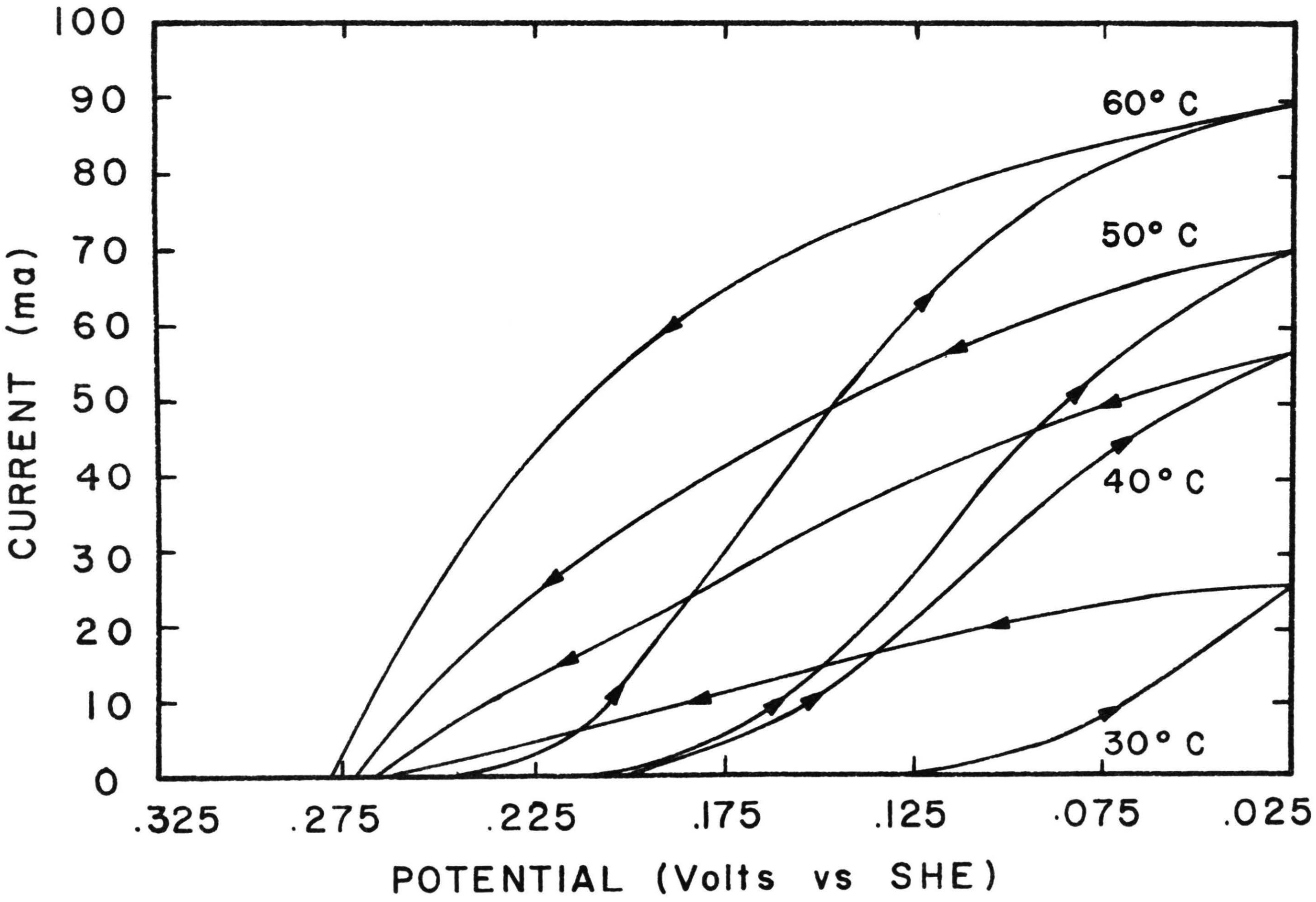

FIGURE 9. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30, 40, 50 AND 60°C. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

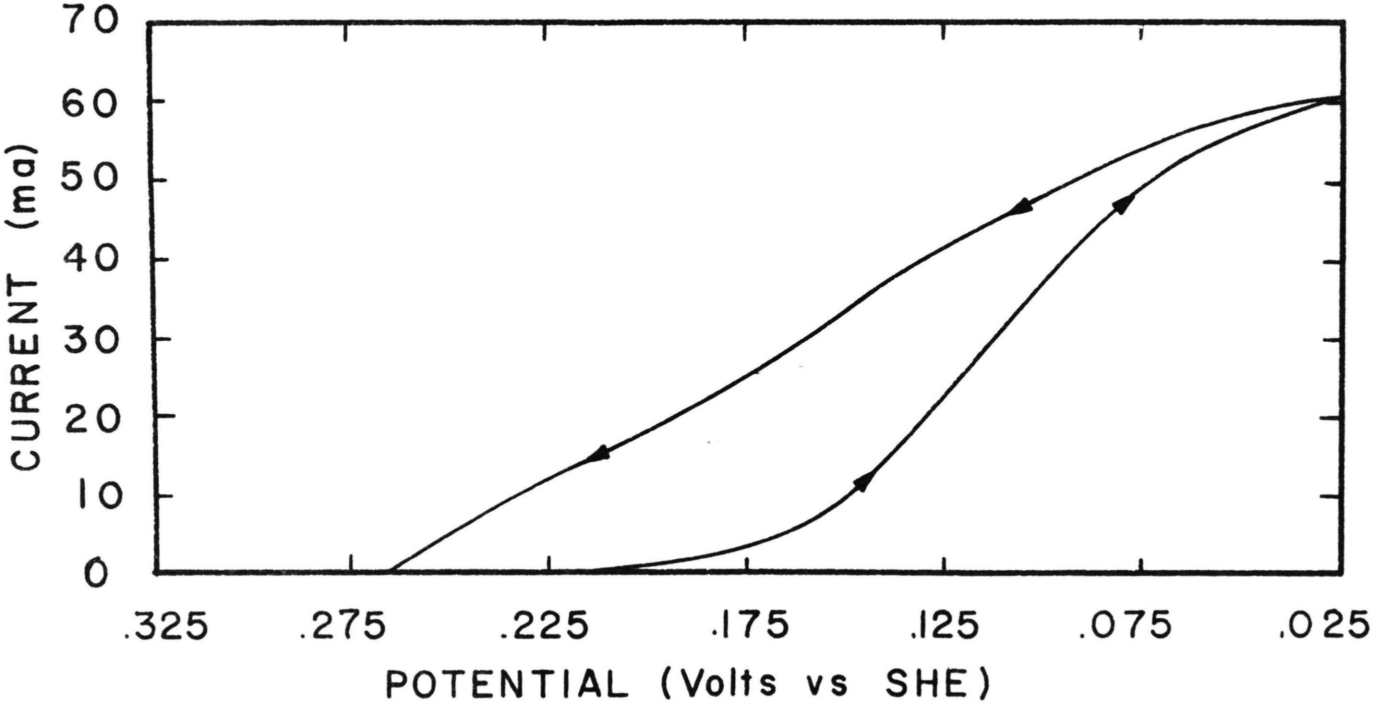

FIGURE 10. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 25 mg/l CHLORIDE ION. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

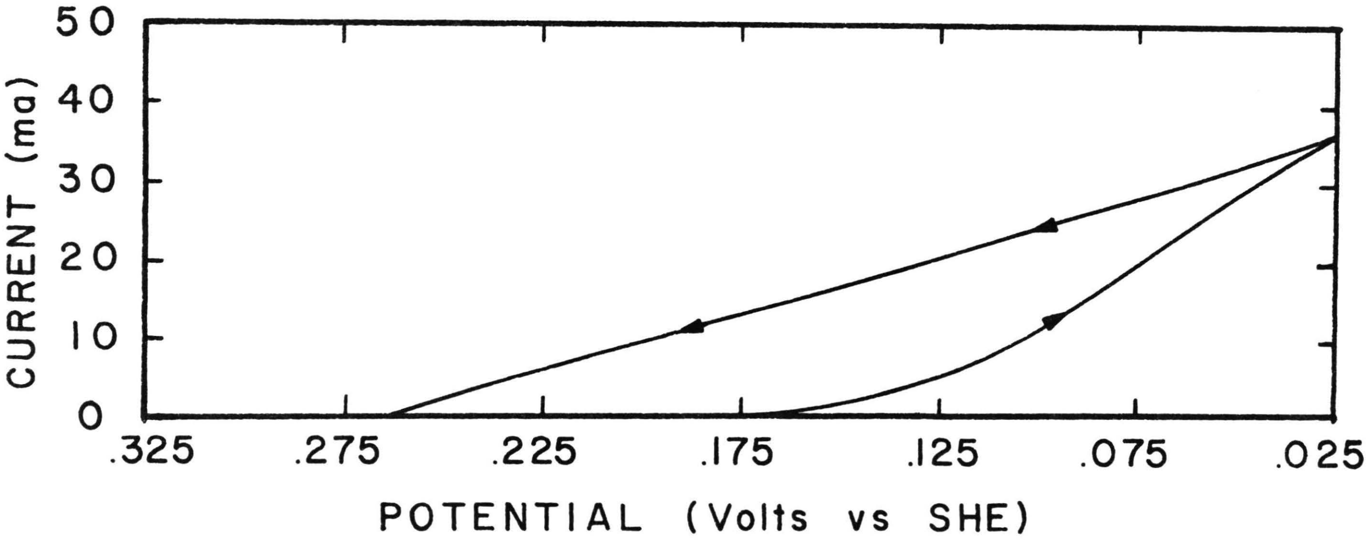

FIGURE 11. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l GLUE. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

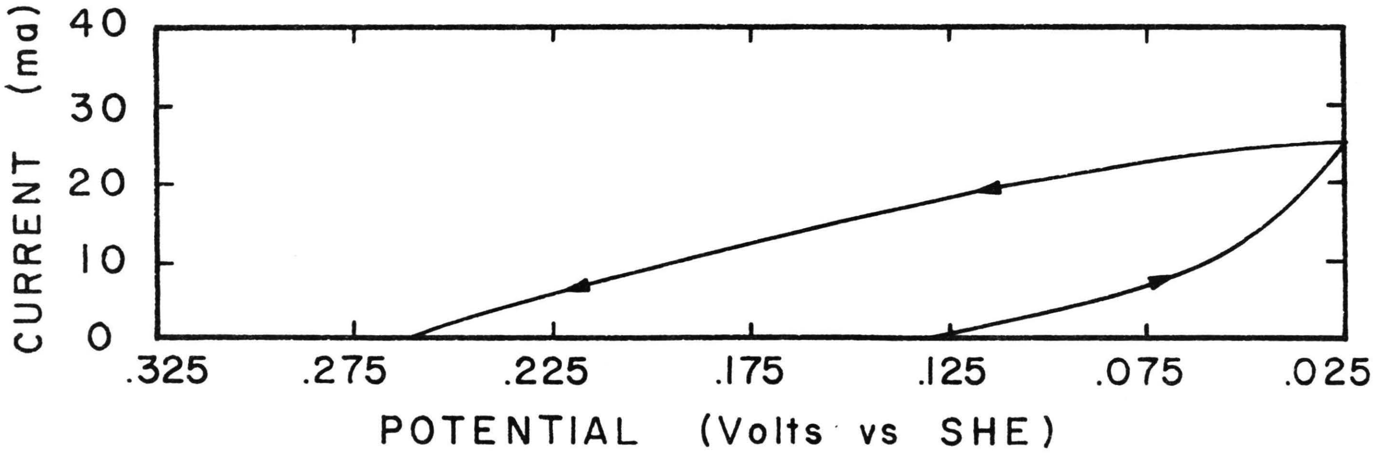

FIGURE 12. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l SEPARAN (DOW NP-10). AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

The effects of concentration changes for these three addition agents, under isothermal conditions, were mixed. The voltammograms did not show any specific trends with regard to polarization and additive concentration. However, increasing the electrolyte temperature at constant additive concentration depolarized the deposition process in a manner similar to the unadulterated solutions.

3. Thiourea Additions. The thiourea-containing solutions produced voltammograms different from the three previously discussed additive solutions. Two types of voltammograms were generated, low temperature (30 and 40°C), Figure 13, and high temperature (50 and 60°C), Figure 14. The cathodic sweeps display distinct inflection points which appeared on all the sweeps except those at 30°C with low thiourea concentration (10 and 25 mg/l). Also, increases in the electrolyte temperature produced more prominent inflection points. The anodic sweeps produced higher currents than the cathodic ones and a small current peak was sometimes present before an abrupt decrease in the anodic current.

C. Deposit Morphologies

1. Copper Cathode. Figures 15 to 17 are typical of electrodeposits obtained on a copper cathode using the unadulterated, glue-or thiourea-containing electrolytes. Only slight changes in the surface morphology were noted

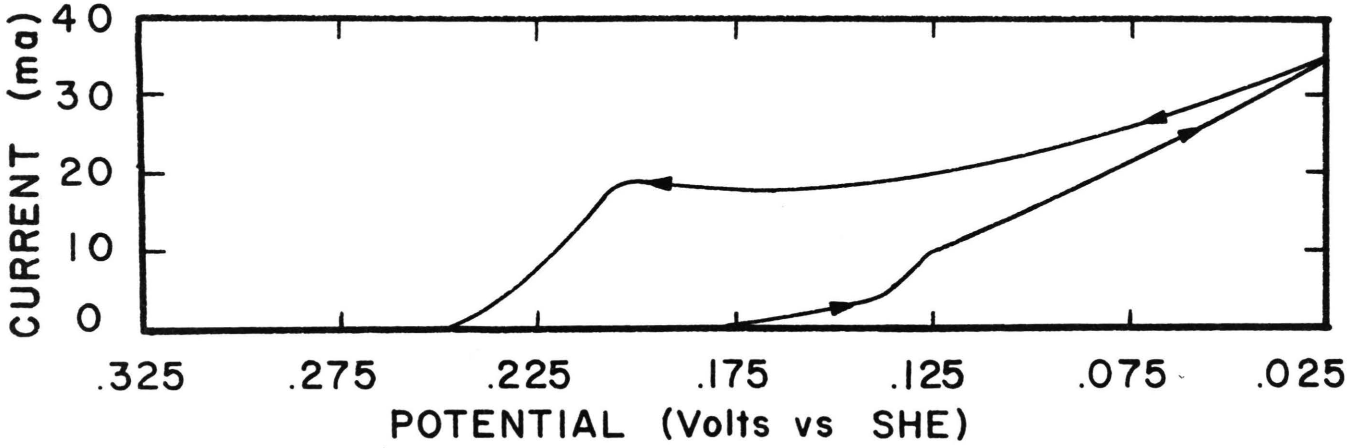

FIGURE 13. VOLTAMMOGRAM FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 25 mg/l THIOUREA. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

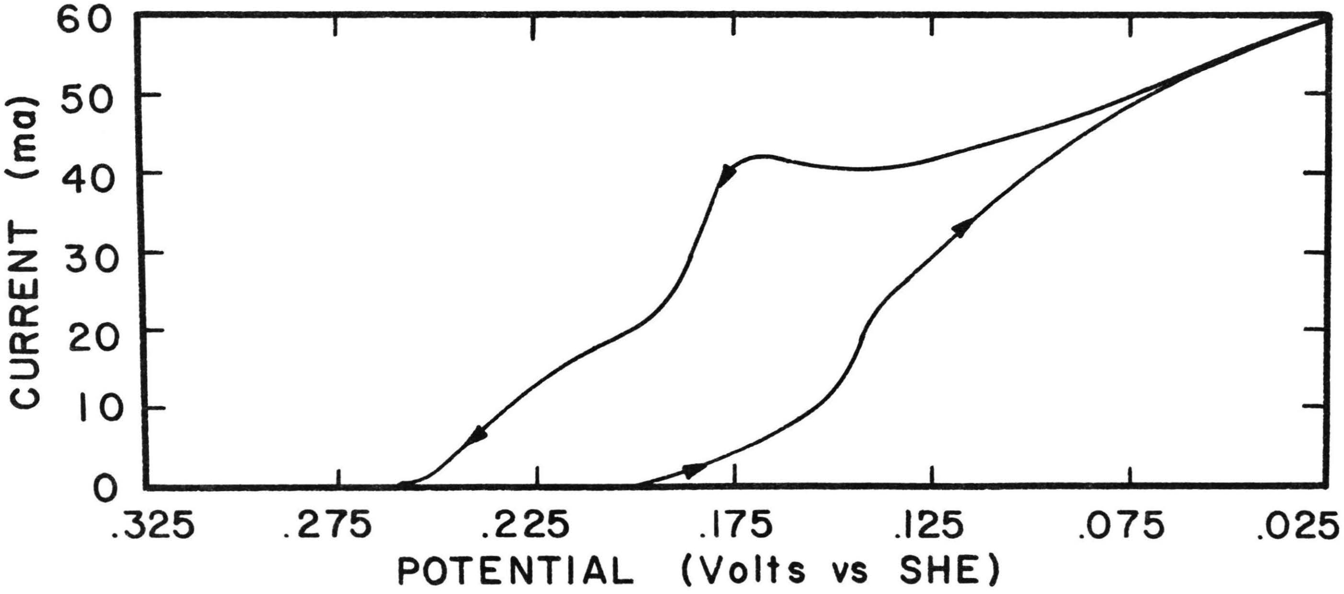

FIGURE 14. VOLTAMMOGRAM FOR ACIDIFIED COPPER ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 50°C CONTAINING 50 mg/l THIOUREA. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

when using this copper substrate. Electrolyzing conditions were 50 mg/l additive concentration and an electrolyte temperature of 40°C. Cathode coverage was very uniform in each and the individual growth crystals were in the range of one micron. The deposit from the unadulterated solution was similar to that for the glue-containing solution except there were some larger crystals, in the five micron range. The thiourea-containing electrolyte produced an electrodeposit with a mixed crystal size and the nodules were more rounded than those from the other electrolytes. In all three deposits, electrogrowth was aligned along striations in the cathode which were produced during the electrode preparation procedure.

2. Titanium Cathode. The morphologies of the copper deposited on the titanium substrate were strongly dependent on both the process variables and the additive present. Distinct and characteristic growth patterns occurred for each additive and notable changes occurred with temperature and concentration variations. Four addition agents, chloride ion, glue, separan and thiourea (at 50 mg/l concentration), at two electrolyte temperatures (40 and 60°C), were used in this part of the investigation. The deposits are shown in Figures 18 to 29.

a. Electrodeposits are 40°C. The unadulterated electrolyte produced a nodular type of growth crystal with

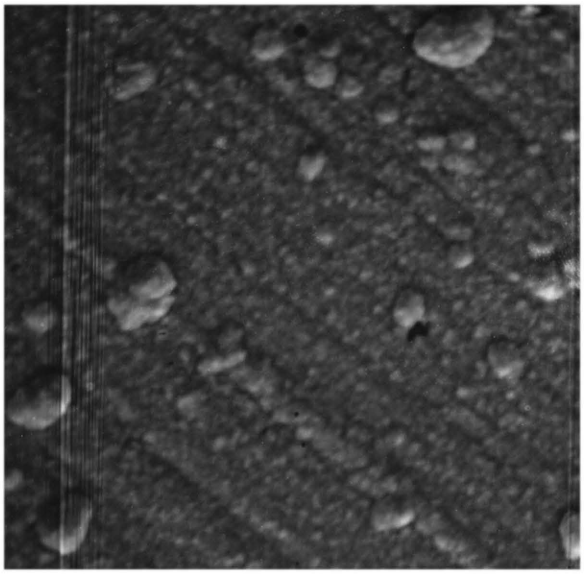

FIGURE 15. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C, Cu CATHODE. 1000x.

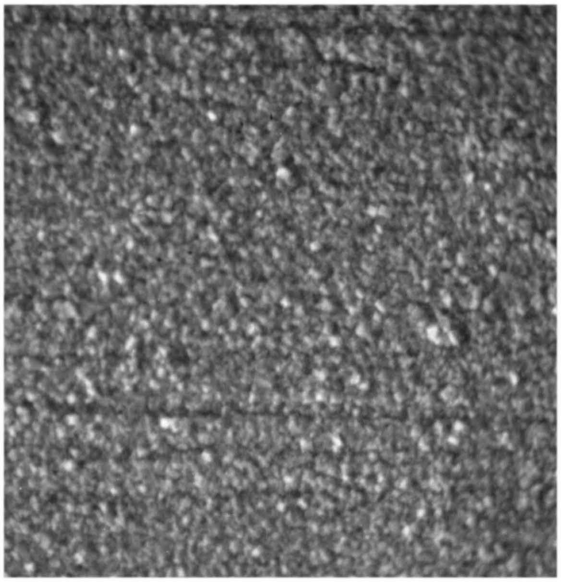

FIGURE 16. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l GLUE. Cu CATHODE. 1000x.

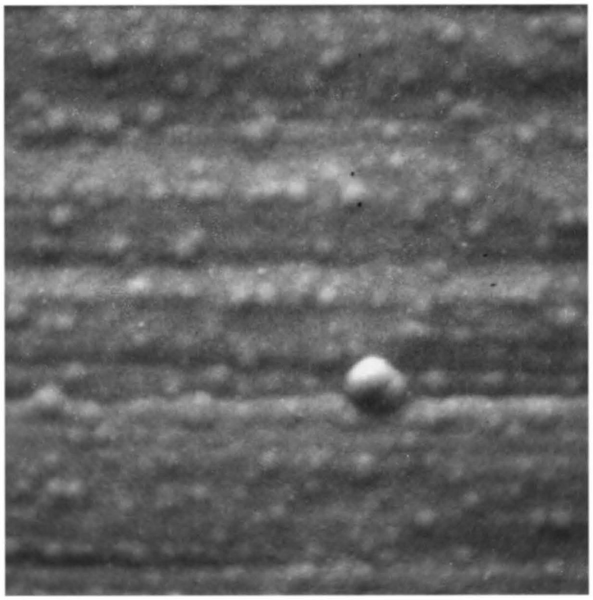

FIGURE 17. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l THIOUREA. Cu CATHODE. 1000x.

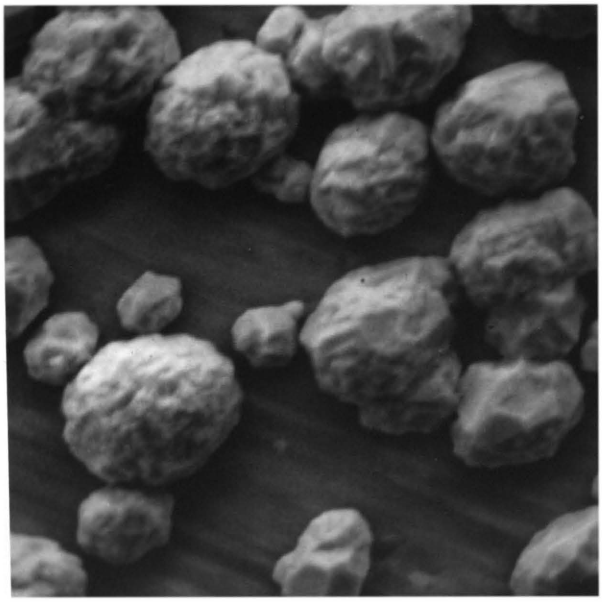

FIGURE 18. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C. Ti CATHODE. 1000x.

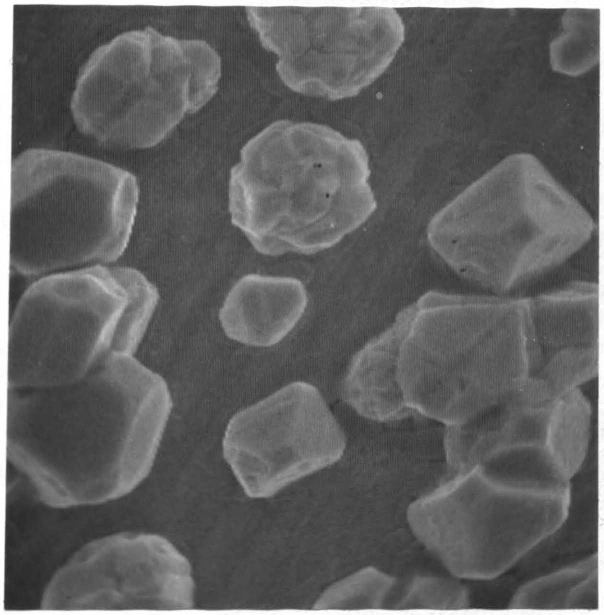

FIGURE 19. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l CHLORIDE ION. Ti CATHODE. 1000x.

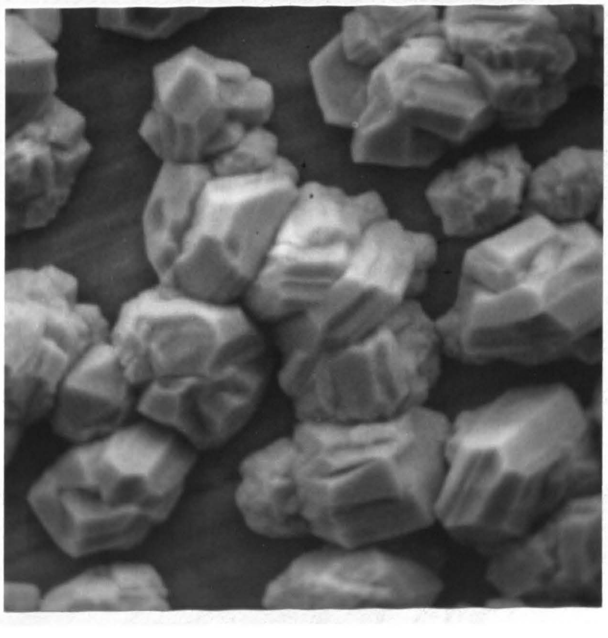

FIGURE 20. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l GLUE. Ti CATHODE. 1000x.

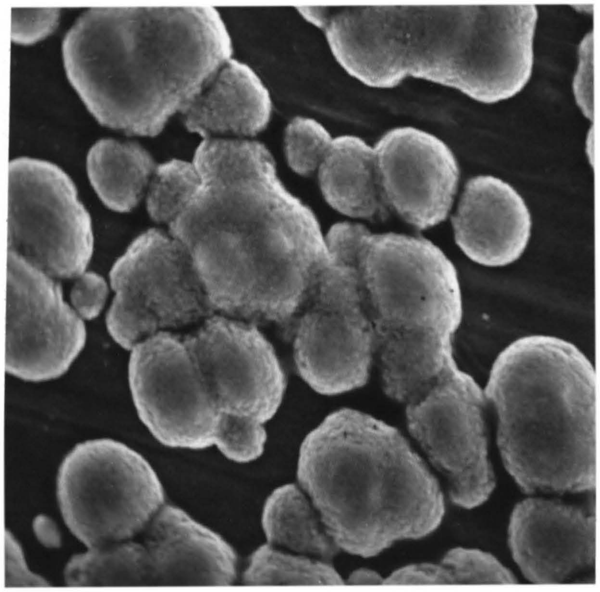

FIGURE 21. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l SEPARAN (DOW NP-10). Ti CATHODE. 1000x.

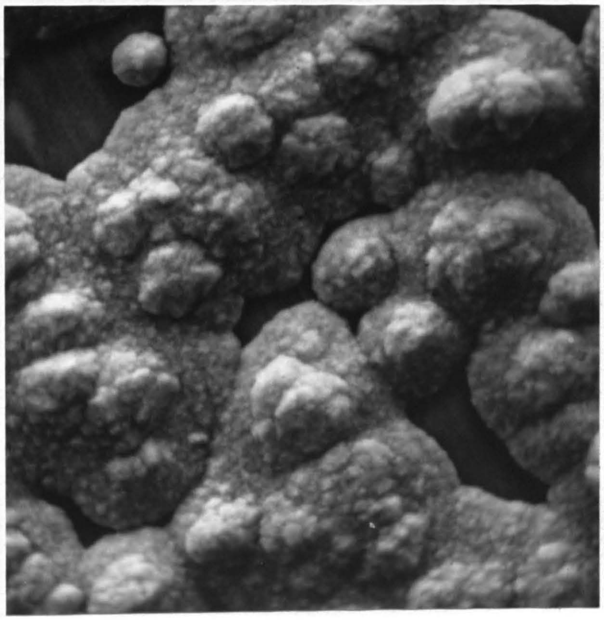

FIGURE 22. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l THIOUREA. Ti CATHODE. 1000x.

a very small facet size. The crystals also exhibited a tendency to grow independently since they were somewhat isolated from each other. No particular orientation could be determined for these growth crystals because of their small facet size and nodular shape. The average size of the larger crystals was 20 microns.

The electrodeposit from the glue-containing electrolyte was characterized by growth crystals that exhibited numerous, well-developed, large facets. A close examination of the faceting revealed a twinning-type mechanism on some of the large crystals. The glue also decreased the amount of independent growth and increased the agglomeration of the crystals.

Electrolyzing the chloride ion-containing solution produced crystals which exhibited two types of symmetry; cubic and pyramidal. There was also a tendency for these crystals to bunch together during growth. In addition to the symmetrical crystals there were a small number of irregularly shaped crystals.

Nodular growth crystals with no identifiable symmetry were the result of electrolyzing the separan-containing solution. Also evident was the bunching of the electrodeposit.

Thiourea growth crystals were quite different from the crystals produced by the previously discussed additions. The electrodeposit was characterized by a central dendritic nucleus with growth progressing laterally across the electrode face to give a continuous copper network. The exact nature of the growth was not determined, but it appeared that the larger central nucleus grew first followed by the lateral growth.

Deposits were also examined with glue-and thiourea-containing solutions at a concentration of 10 mg/l. Figures 23 and 24 show these particular electrodeposits. The morphologies were similar to those at 50 mg/l, except the crystals from the glue solution were smaller. The electrodeposit from the thiourea solution had a more extensive lateral growth and electrode coverage than at the higher concentration.

b. Electrodeposits at 60°C. Nodular growth crystals, 15 to 20 microns, with an irregular facet size were the most prominent type produced by the unadulterated electrolyte. However there were also a few symmetrical crystals with well-defined facets. The overall growth mode of these crystals again seemed to be from a single initial nucleation point.

The glue-containing electrolyte produced crystals with mixed sizes ranging from 10 to 20 microns. The larger crystals exhibited well-developed and defined facets with no distinct orientation. The smaller crystals were nodular with a more irregular pattern of faceting. A large number of crystals grew independently

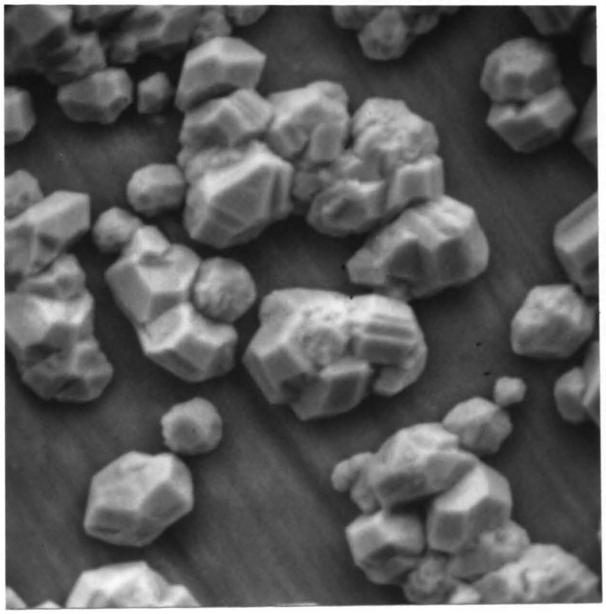

FIGURE 23. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 10 mg/l GLUE. Ti CATHODE. 1000x.

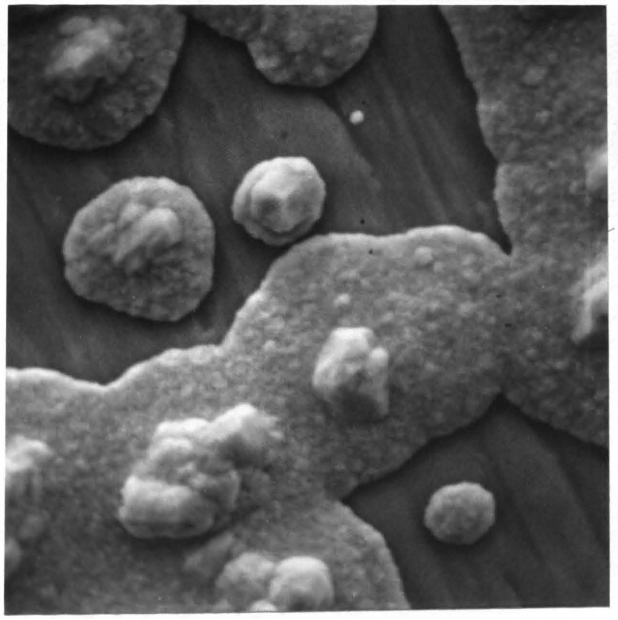

FIGURE 24. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 10 mg/l THIOUREA. Ti CATHODE. 1000x.

of each other but there was some tendency for clustering.

Symmetrical cubic and pyramidal crystals were an obvious characteristic from electrolyzing the chloride ion-containing solution. A few nodular-type growth crystals were also present. The pyramidal growth crystals did not appear to exist singly but rather were a growth extension of a cubic-type crystal. The average size of the crystals was: cubic, 15 to 20 microns and pyramidal, 10 to 15 microns.

The separan-containing electrolyte, at this higher temperature, produced nodular crystals ranging in size from, 10 to 20 microns, with a small facet size. While there was a tendency for individual growth, there was also a definite bunching of several neighboring growth crystals. Some symmetrical growth crystals with well-developed facets were also present but they were few in number.

The thiourea-containing solution produced a nodular-type of growth crystal, ranging in size from 5 to 20 microns, with a very fine facet size. There was no lateral growth at this higher temperature but neighboring growth crystals did show some agglomeration. Also there was no identifiable symmetry associated with these particular crystals.

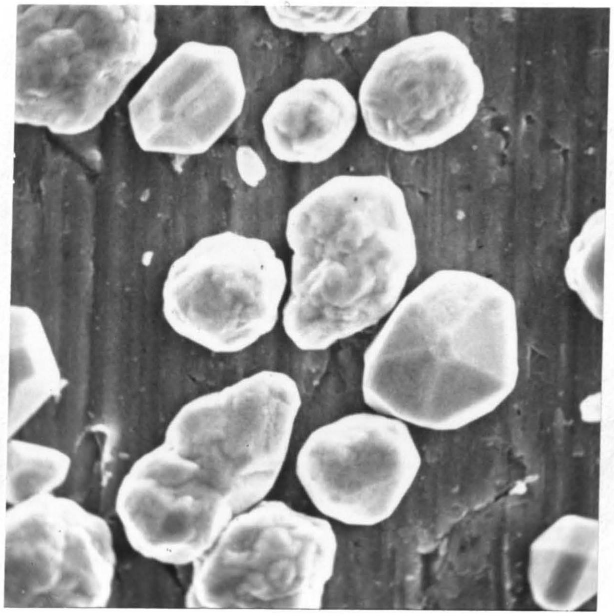

FIGURE 25. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C. Ti CATHODE. 1000x.

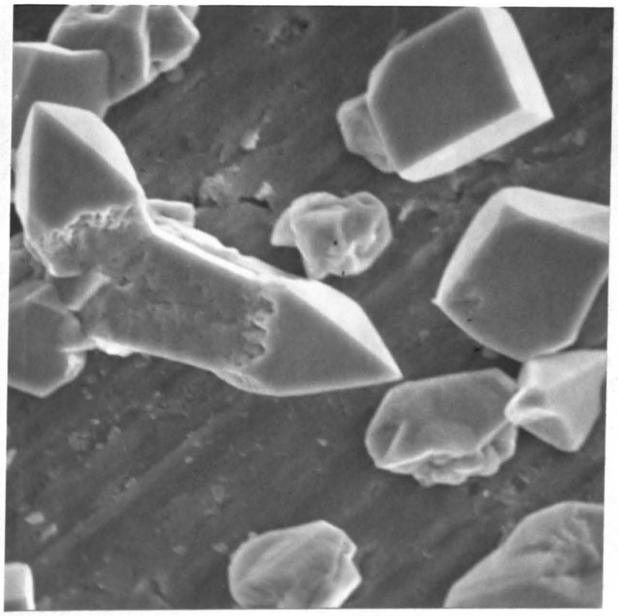

FIGURE 26. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l CHLORIDE ION. Ti CATHODE. 1000x.

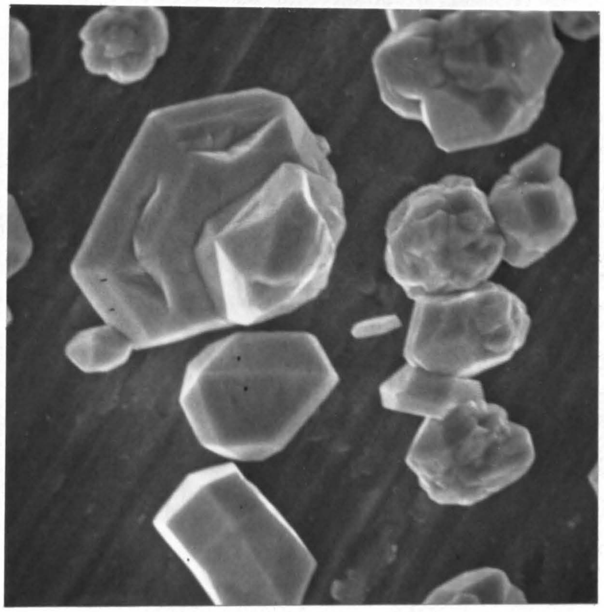

FIGURE 27. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l GLUE. Ti CATHODE. 1000x.

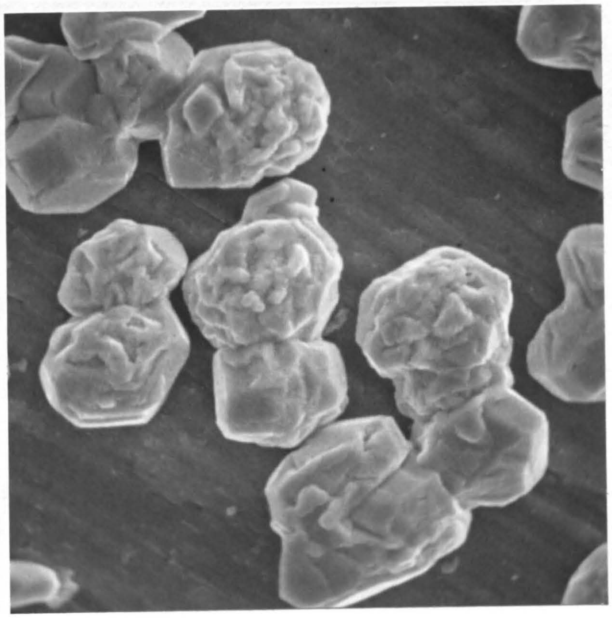

FIGURE 28. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l SEPARAN. Ti CATHODE. 1000x.

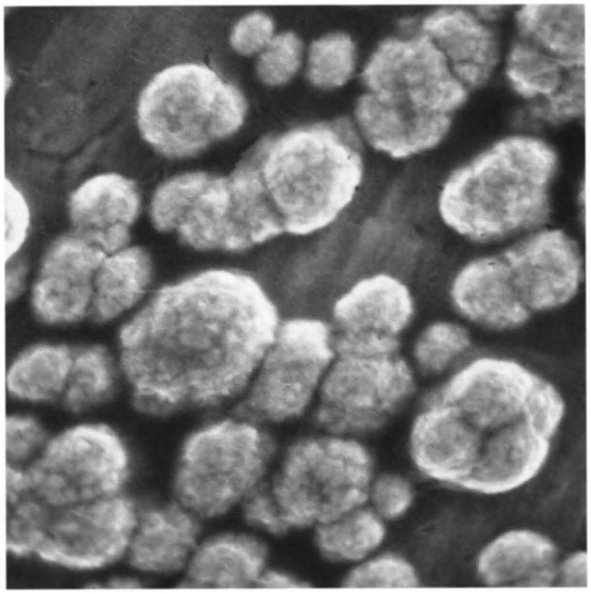

FIGURE 29. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l THIOUREA. Ti CATHODE. 1000x.

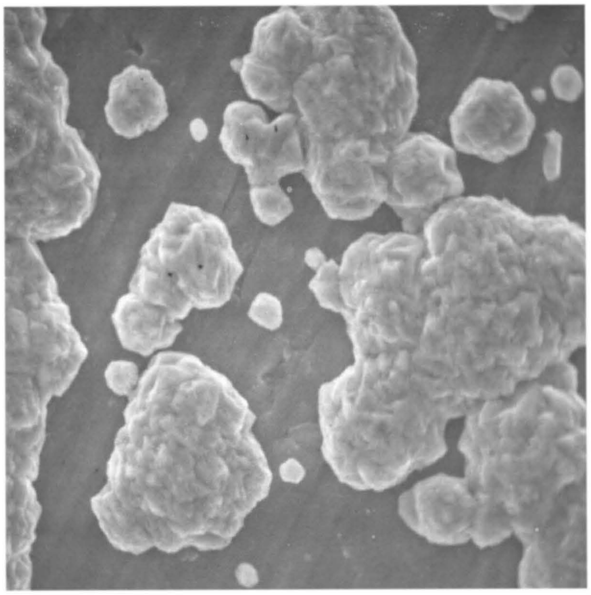

FIGURE 30. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l CHLORIDE ION AND 50 mg/l SEPARAN. Ti CATHODE. 1000x.

Solutions with several addition agent combinations were electrolyzed to determine if synergistic effects existed among the additives and to determine which would predominate in the growth mechanism.

c. Additive Combination Electrodeposits at 40°C. The structures resulting from electrolyzing the chloride ion-separan or glue-separan combinations (each additive at 50 mg/l) at 40°C are shown in Figures 30 and 31. The electrodeposits were characteristized by large, agglomerated crystals possessing a small facet size. The overall degree and type of faceting of the crystals were characteristic of a 40°C separan morphology, and there was little evidence of any glue or chloride ion influence.

d. Additive Combination Electrodeposits at 60°C. Chloride ion-thiourea, chloride ion-glue or chloride ion-separan combinations (each at 50 mg/l) were electrolyzed at 60°C. The resulting deposits are shown in Figures 32, 33 and 34. Each particular combination produced growth crystals with well-developed facets and bunching of the deposits was evident. The chloride ion-thiourea and chloride ion-glue combinations appeared to be more influenced by the chloride ion but the chloride ion-separan deposit had a structure more characteristic of a 60°C separan morphology. Especially

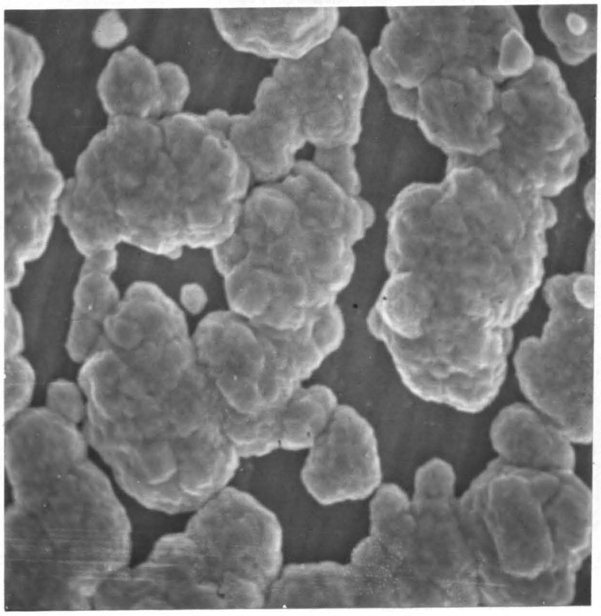

FIGURE 31. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 50 mg/l SEPARAN AND 50 mg/l GLUE. Ti CATHODE. 1000x.

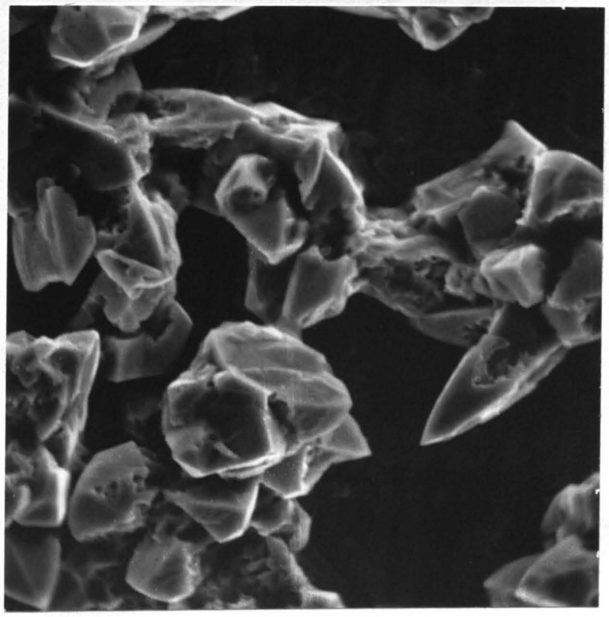

FIGURE 32. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l CHLORIDE ION AND 50 mg/l THIOUREA. Ti CATHODE. 1000x.

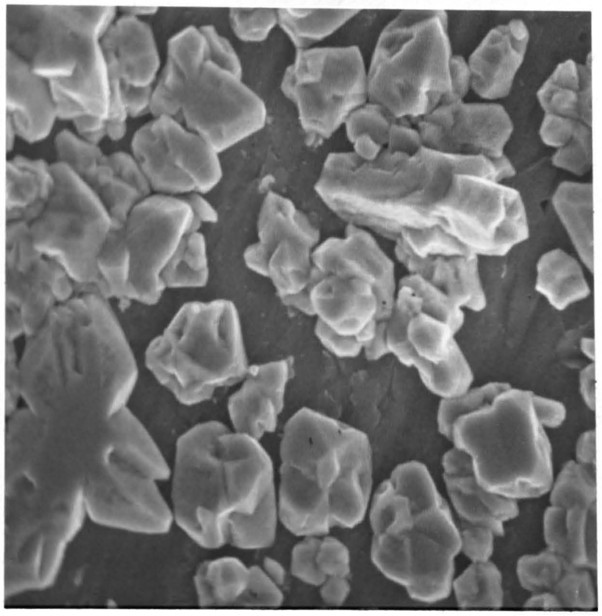

FIGURE 33. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l CHLORIDE ION AND 50 mg/l GLUE. Ti CATHODE. 1000x.

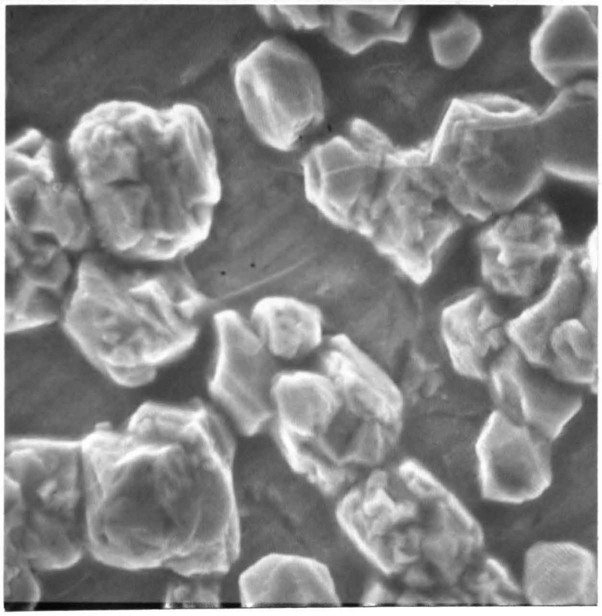

FIGURE 34. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 50 mg/l CHLORIDE ION AND 50 mg/l SEPARAN (DOW NP-10). Ti CATHODE. 1000x.

noticeable on the chloride ion-thiourea deposit were the pyramidal crystals characteristic of chloride ion-containing solutions.

IV. RESULTS AND DISCUSSION

The experimental results were examined to determine if the effects of the various addition agents could be differentiated by voltammetry and scanning electron microscopy. Specifically, reproducible correlations were sought with different process parameters that would exemplify modifications in the polarization behavior or the morphology of the electrodeposits. The parameters which were given primary emphasis were the type and concentration of the additive and the electrolyte temperature.

In the course of the investigation it was found that the presence and electroactivity of one particular additive might be delineated in the cathodic sweep whereas another might be better characterized during the anodic sweep. Also, certain other variations in polarization behavior were noted to occur with changes in the electrolyte temperature. Therefore, data had to be obtained from a series of experiments or scans in which the variables were altered, before a meaningful analysis could be made.

A. Copper Cathode

1. Unadulterated, Glue and Separan Additions. Illustrated in Figure 35 are the copper cathode, anodic sweep curves at 40 and 60°C using unadulterated, glue-or separan-containing solutions. Other temperatures and

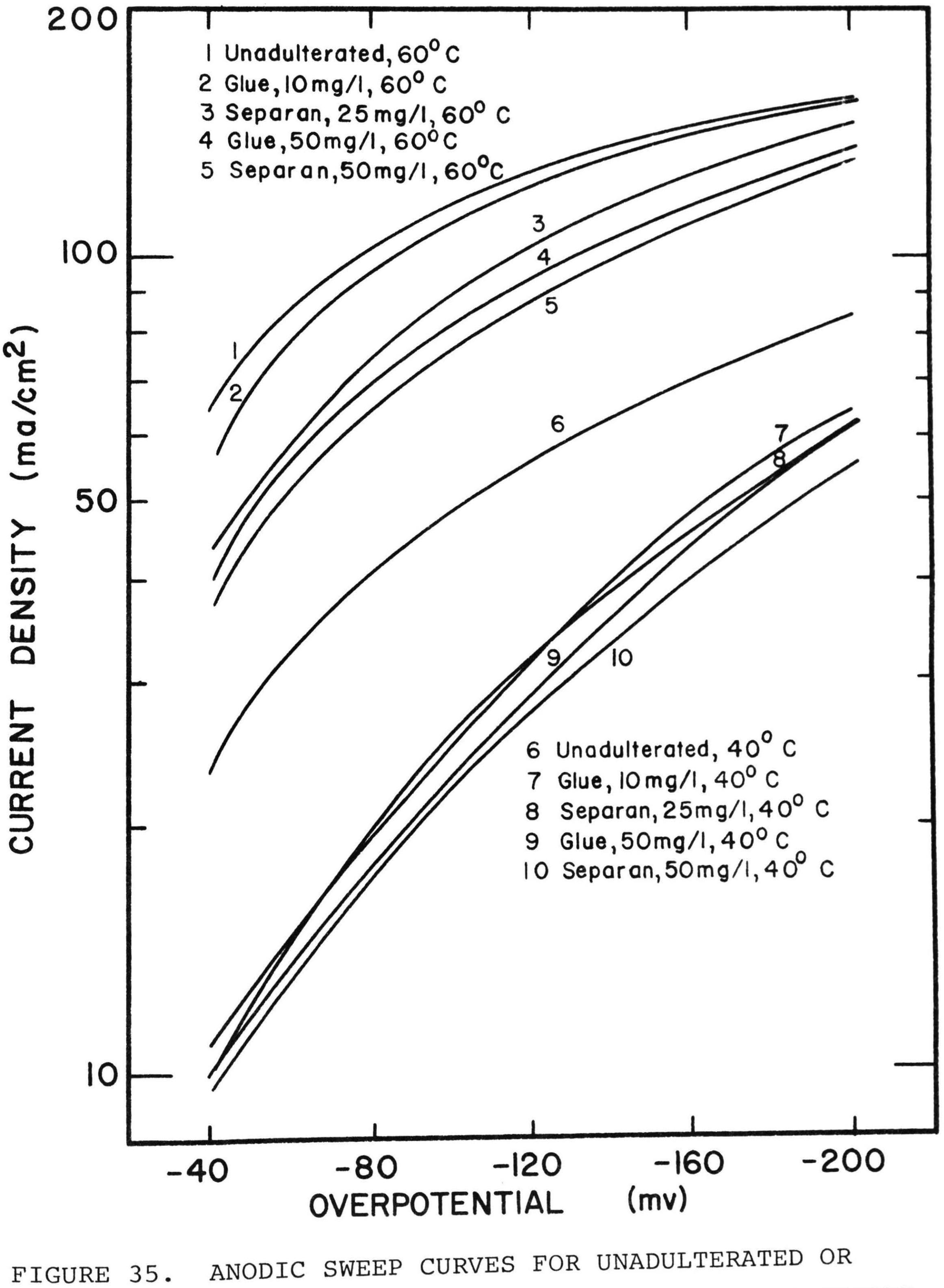

FIGURE 35. ANODIC SWEEP CURVES FOR UNADULTERATED OR ORGANIC ADDITIVE CONTAINING ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40 and 60°C. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

concentrations were also used, but these curves were representative of the overall polarization behavior. The anodic sweeps because they were more reproducible, were used to show the organic additive effects rather than the cathodic sweeps. These anodic sweeps were more reproducible since there was less influence from original copper substrate and any oxide films or impurities initially present on the surface. Also, for the anodic sweeps a freshly electrodeposited copper surface was present, and therefore the results were free of initial nucleating effects. The cathodic sweeps did show the same basic trends as the anodic ones however.

At 40°C the organic additives, glue and separan, substantially increased the electrolysis polarization, compared to the unadulterated electrolyte, but the relative degree of polarization was not appreciably affected by increasing the electrolyte additive content. However, with increasing electrolyte temperature, the relative degree of polarization was much more susceptible to the electrolyte additive concentration. Figure 36 further illustrates the current density-concentration relationship for glue at 30 and 60°C.

The lower current densities which resulted when glue or separan were present in the electrolyte, were due to the typical actions ascribed to organic additives, viz, adsorption, film formation and inhibition. Also, at all temperatures the polarization curves did not exhibit any

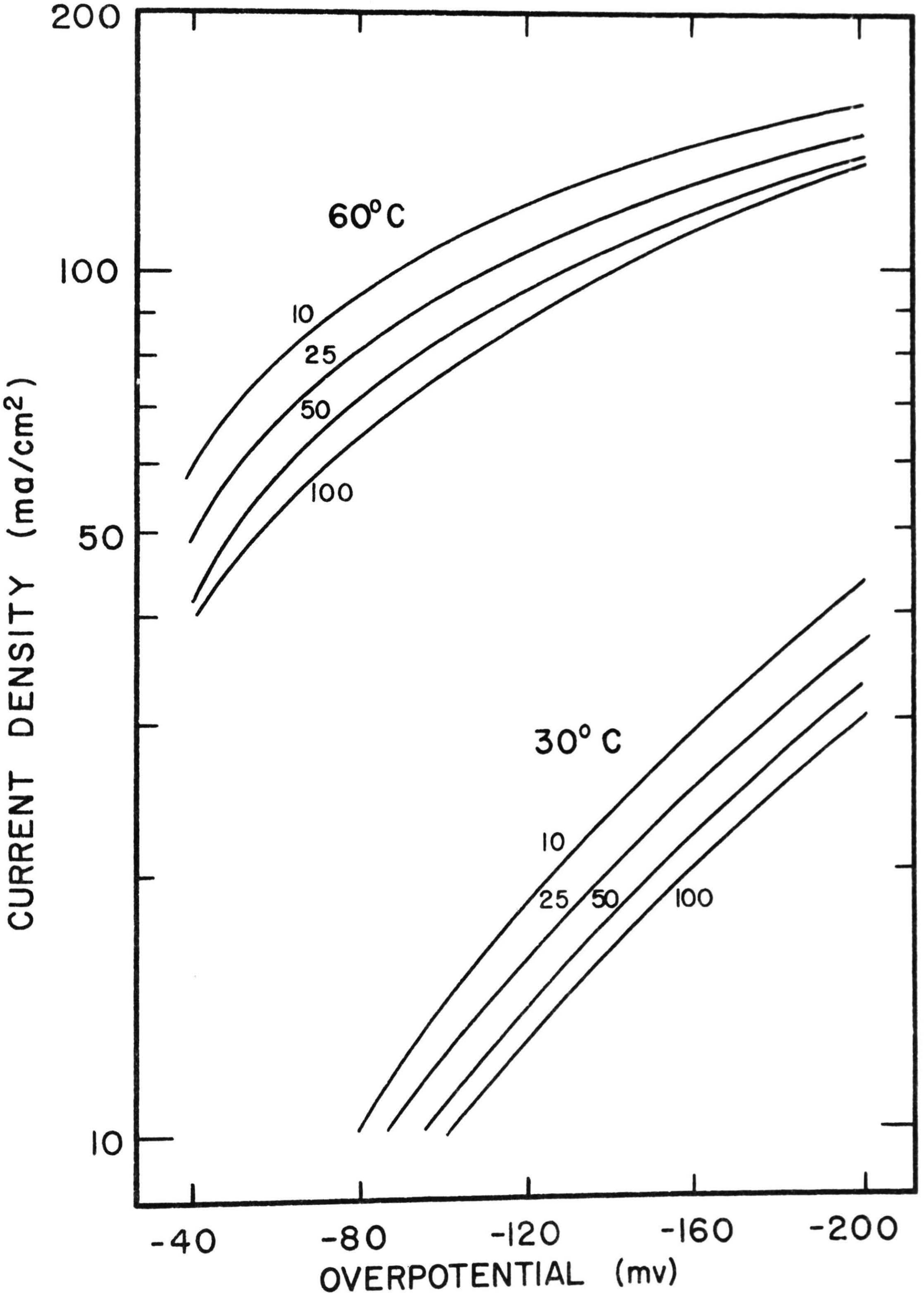

FIGURE 36. ANODIC SWEEP CURVES FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30 AND 60°C CONTAINING 10, 25, 50 OR 100 mg/l GLUE. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

marked inflection points, therefore no major change in the metal deposition mode occurred over the overpotential range studied.

Thus evaluations of changes in the polarization curves with temperature should indicate the presence and concentration of an organic additive. It should be recognized that this type of evaluation is relative in nature, and requires systematic comparisons between "pure solutions", or ones known to yield satsifactory results, and the "unknown" or plant solutions being processed at any given time. Other means of evaluation, such as deposit morphology would be required to delineate the specific type of electroactive organic, assuming that more than one is present.

2. Chloride Ion Additions. The cathodic and anodic sweeps from the chloride ion-containing electrolytes produced current densities substantially lower than the three previous solutions. This behavior was characteristic of all chloride ion-containing solutions and Figure 37 illustrates the anodic sweep curves at 40 and 60°C, with 10 mg/l of chloride ion. (The unadulterated and glue curves were placed on the figure to put the low chloride ion current densities into perspective.) Thus, the chloride ion acted as an inhibitor, at least during these short time voltage scans; the inhibiting effect

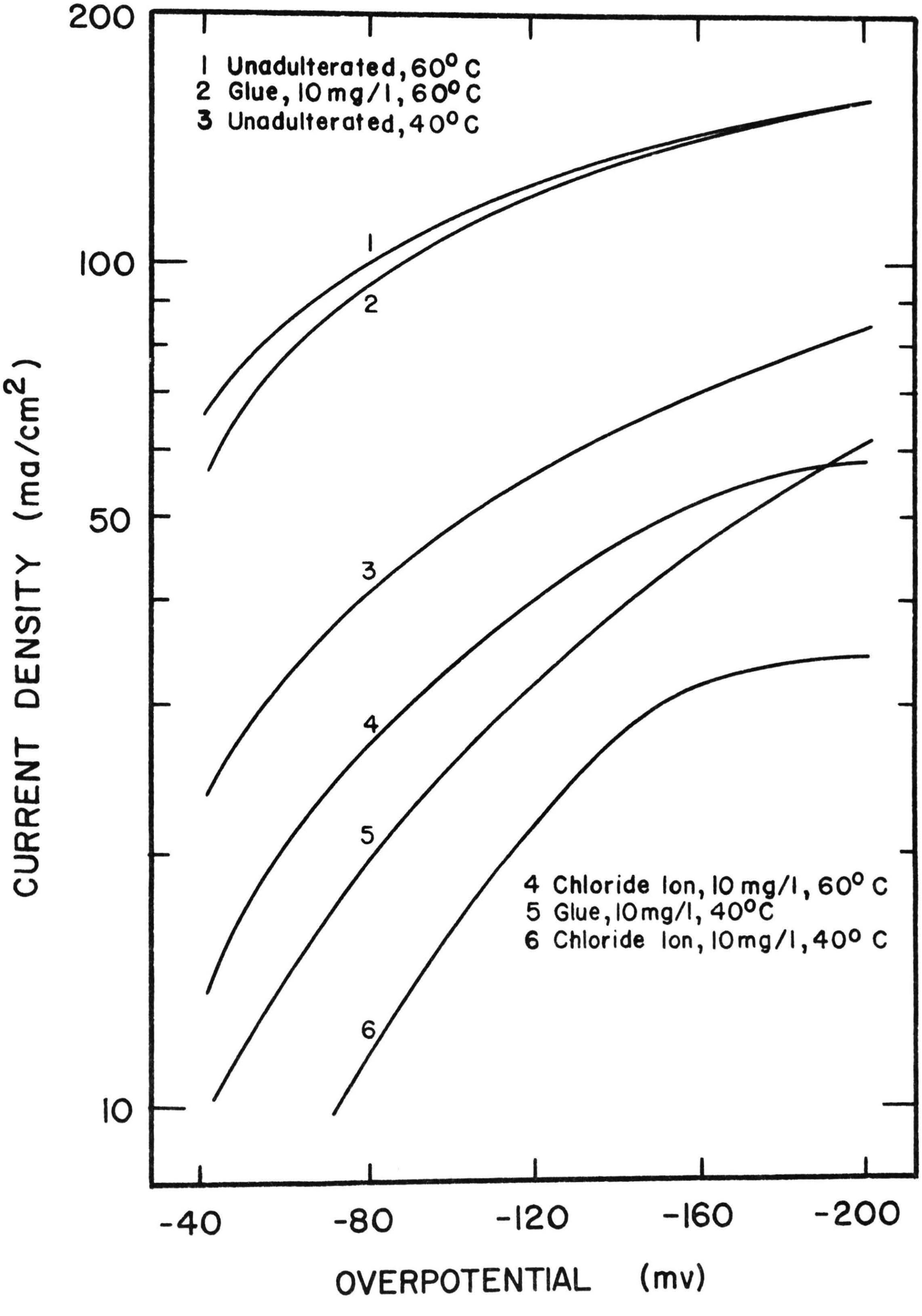

FIGURE 37. ANODIC SWEEP CURVES FOR UNADULTERATED, GLUE OR CHLORIDE ION CONTAINING ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40 AND 60°C. AREA COPPER CATHODE =

was due to the formation of a copper chloride film on the cathode. Also, since both the cathodic and anodic sweeps of the chloride ion voltammograms traced the same paths, it could be assumed that the film remained stable, or continued to form and affect the polarization behavior, up to overpotentials as high as -200 mV. Therefore, if the chloride ion was the electroactive species in the electrolyte it could possibly be detected by the large degree of polarization it produces, particularly with increasing temperature. Again, other means of evaluation must be employed to definitely determine that the chloride ion was the electroactive species.

3. Thiourea Additions. Illustrated in Figure 38 are representative cathodic sweep curves for thiourea-containing solutions at various tempertures and concentrations. The scans from the 10 mg/l thiourea-containing electrolytes exhibited the distinct current maximums which were indicative of some type of reduction reaction. At 30, 40 and 50°C, the peak was well defined, whereas at 60°C the peak was present but considerably broader and with a diminished height.

Analysis of the experimental evidence suggests that upon insertion of the copper electrode into the electrolye, a complex film, most likely consisting of copper and sulfur, formed on the cathode. This film, which appeared

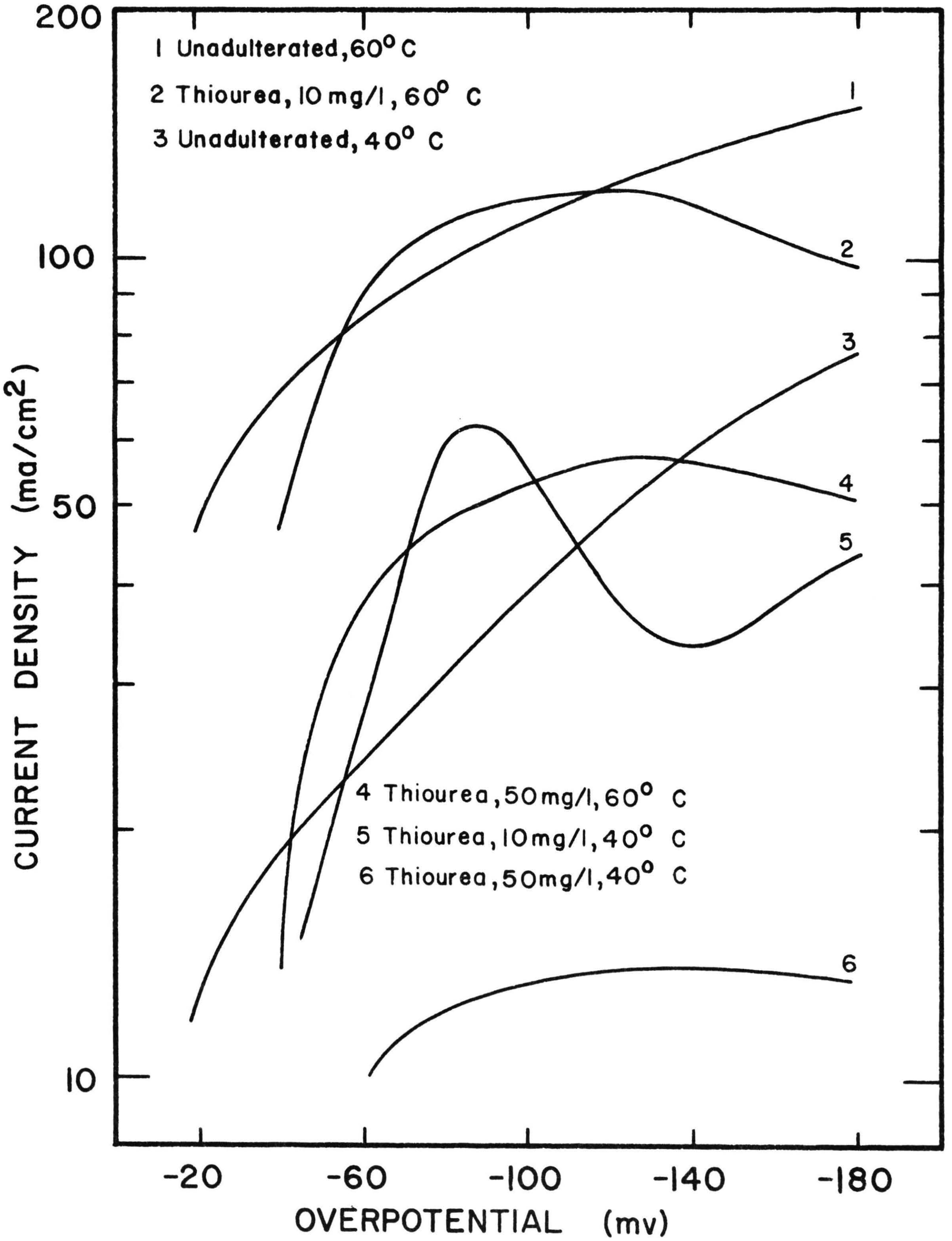

FIGURE 38. CATHODIC SWEEP CURVES FOR UNADULTERATED OR THIOUREA CONTAINING ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40 AND 60°C. AREA OF COPPER CATHODE = 1.26 cm^2. SCAN RATE = 1 mV/sec.

unstable at overpotentials greater than approximately -135 mV, reacted under the influence of the applied potential resulting in the current peak. The exact composition of this film was not determined but many chemical variations are possible. Besides the regular cupric and cuprous sulfides both Cu_7S_4 and Cu_9S_5 have been identified in copper sulfide electrolysis [14], and there are also non-stoichiometric compositions to be considered.

Scanning electron photomicrographs (Figures 39 and 40) were taken of copper electrodeposits from an unadulterated electrolyte and an electrolyte containing 10 mg/l thiourea. The electrodeposits were produced by cathodically scanning to -135 mV overpotential and immediately removing the electrode from the electrolyte for examination. The electrodeposit from the thiourea-containing solution exhibited a smaller particle size than the deposit from the unadulterated solution, and this size difference can possibly be attributed to the interaction of a copper-sulfur film with the electrogrowth process. Alterations in the nature of the film during the voltage scan could change the electrode surface area or perhaps additional nucleation sites could be provided. A smaller particle size would result in either case.

The cathodic sweeps of voltammograms produced with electrolytes containing 25 mg/l or greater thiourea exhibited the extensive current plateaus which were

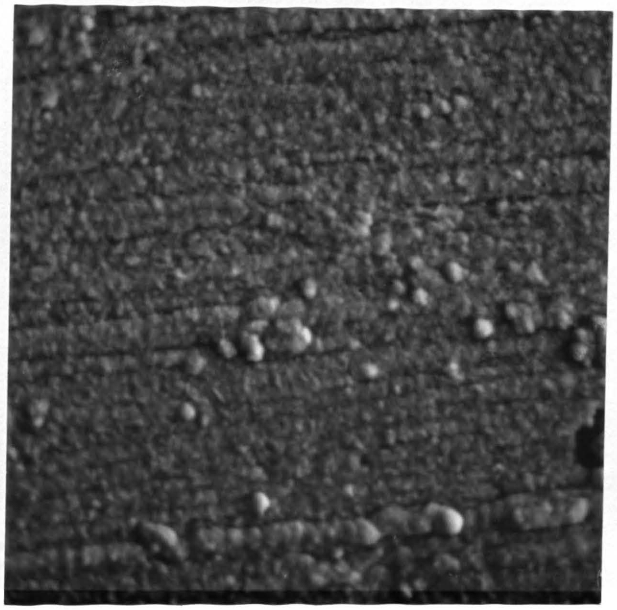

FIGURE 39. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C. COPPER CATHODE. 1000x.

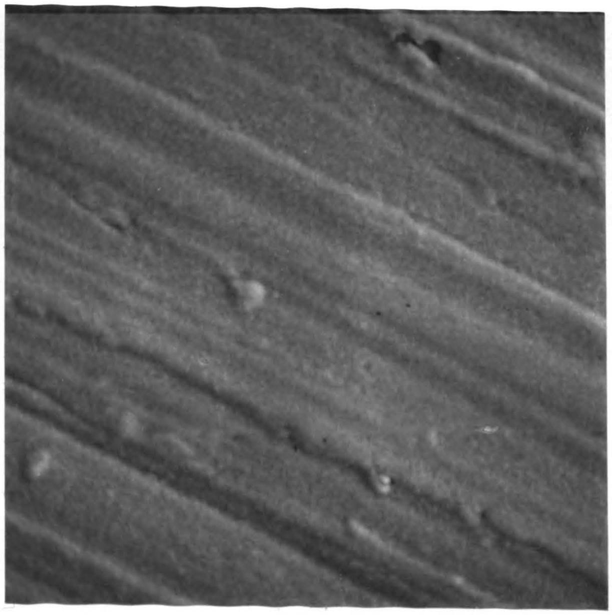

FIGURE 40. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C CONTAINING 10 mg/l THIOUREA. COPPER CATHODE. 1000x.

indicative of a passive film on the cathode. Also, the values of the limiting current were decreased with increasing thiourea concentration. This indicated that the film formed was probably cathodically adsorbed and the degree of coverage or thickness attained was a function of the amount of thiourea available. Kabanov [14] had observed similar polarization curves for tin electrolysis. He ascribed the limiting current plateau to strong cathodic adsorpiton of electrolyte surfactants, and only upon attainment of a high cathodic overpotential could the adsorbed layer be disrupted, permitting the sharp current increase.

On all the anodic sweeps, regardless of thiourea concentration or temperature, there was always a prominent feature exhibited (e.g. plateau, peak) in the overpotential range where the cathodic current peak occurred. These features were most probably due to the reformation of some type of copper-sulfur film. Also, at higher temperatures the current density decreased with increasing thiourea concentration.

The basic nature of the cathodic film formed with the thiourea-containing electrolytes showed a strong dependence on the concentration of the additive, which could have resulted from alterations in the film composition and structure. The film formed with low thiourea concentrations reacted cathodically, whereas at high thiourea concentrations, the nature of the film was altered sufficiently, so that it remained stable over a large overpotential range.

Based on these results, it seems that the characteristic thiourea current peak or current plateau would provide a means of detecting the presence of thiourea in a copper electrolyte. Furthermore, at high temperatures, the value of the anodic sweep current density could be used to estimate the effective concentration of thiourea in solution.

B. Titanium Cathode

1. Polarization and Temperature Effects Upon Copper Electrodeposit Morphologies.

The titanium cathode electrodeposits (Figures 18-22, 25-29) showed a decreased facet size with increased polarization for all solutions except those containing glue. Typical polarization curves are shown in Figures 41 and 42. As the degree of polarization increased, the electrodeposit facet size decreased but without any apparent effect on the copper crystal electrode coverage. Thus, the additives directly influenced the crystal growth and polarization behavior during electrolysis but not the initial degree of nucleation. At 40°C, the degree of polarization increased in the order; separan>thiourea>unadulterated>chloride ion with increased facet size

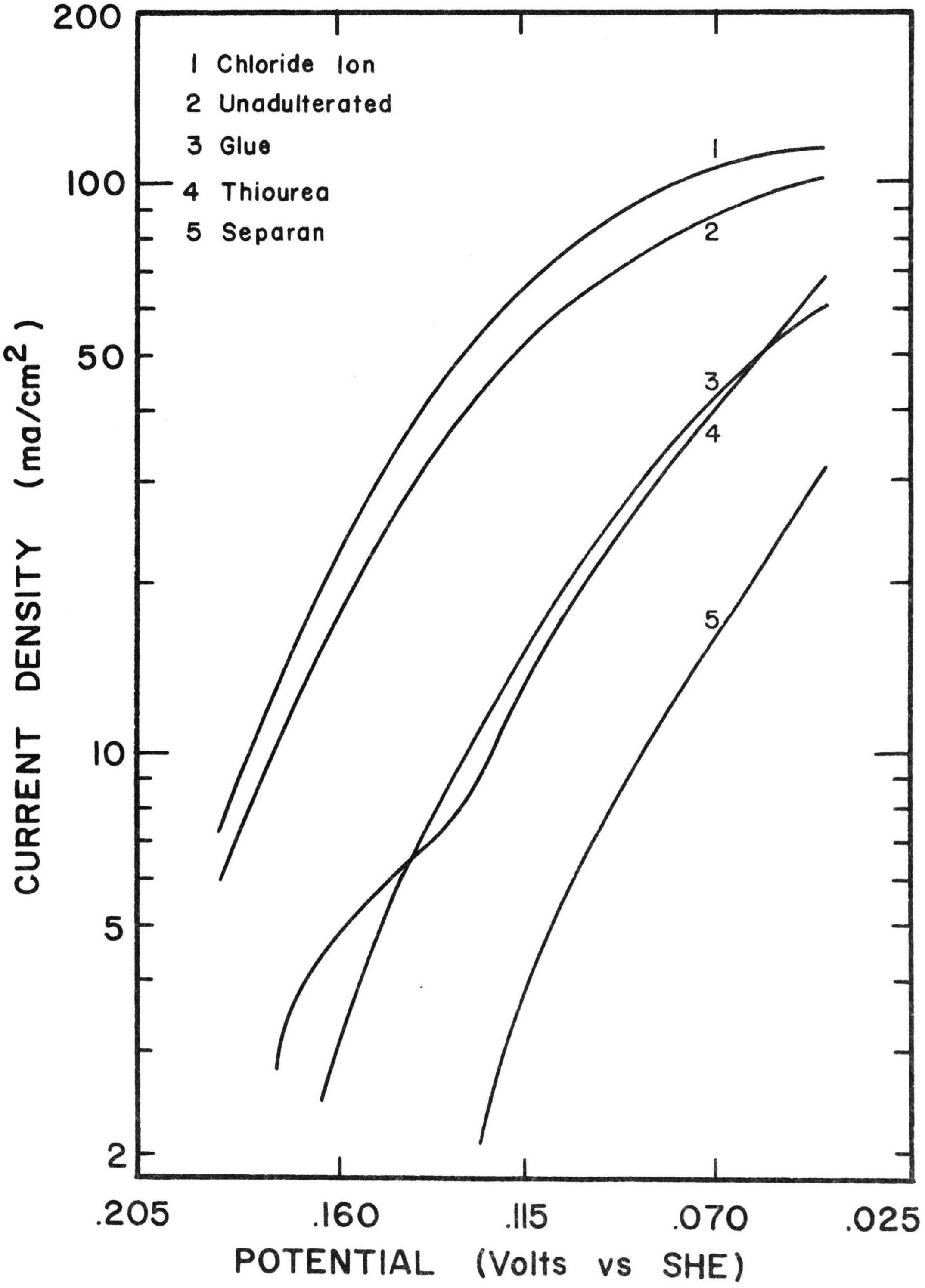

FIGURE 41. CATHODIC SWEEP CURVES FOR UNADULTERATED OR ADDITIVE CONTAINING (50 mg/l ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C. TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

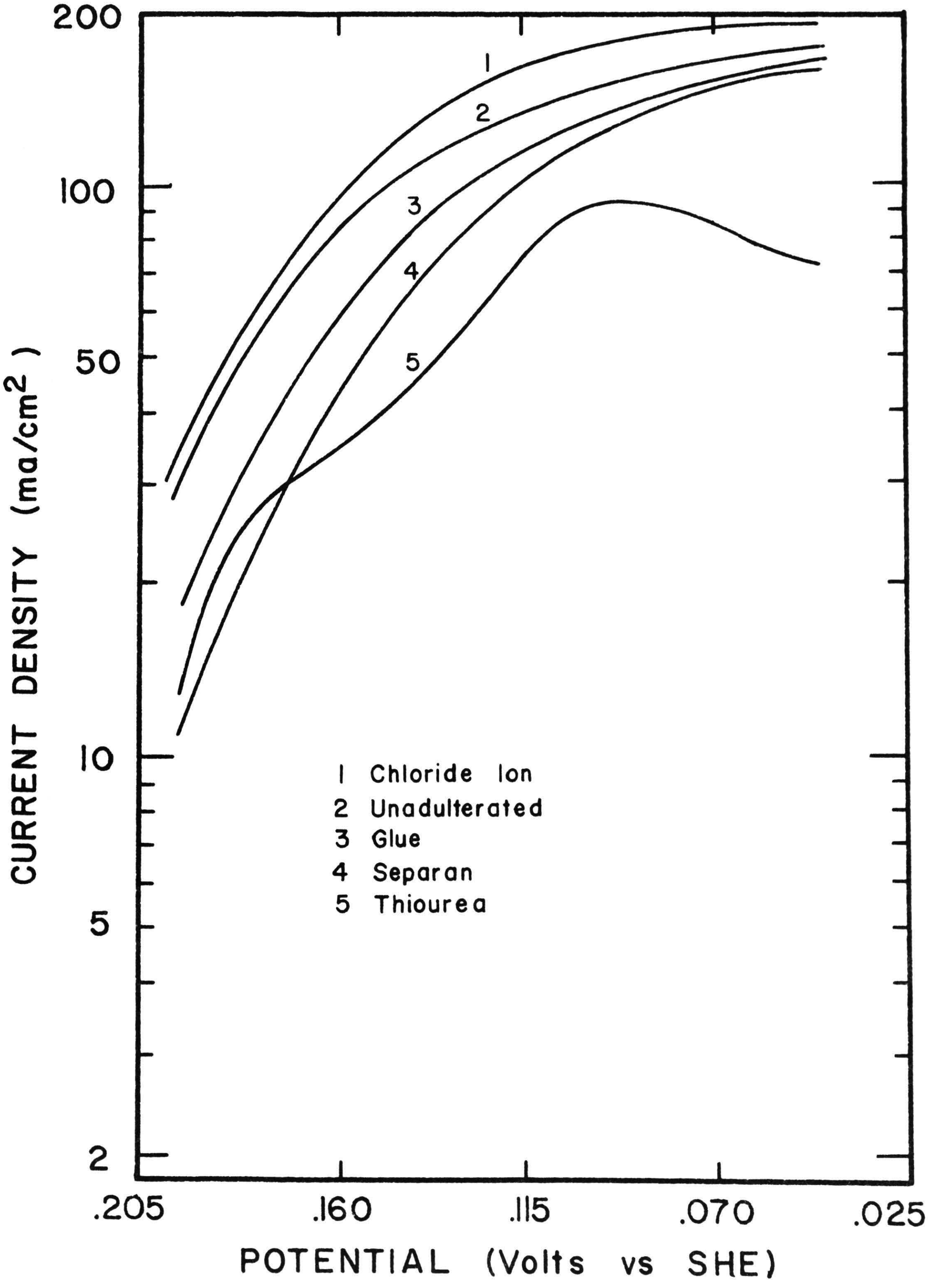

FIGURE 42. CATHODIC SWEEP CURVES FOR UNADULTERATED AND ADDITIVE CONTAINING (50 mg/l) ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

occurring in the same order. The separan-containing solution produced crystals with an extremely fine facet size while the chloride ion-containing solution, produced cubic and pyramidal crystals with the largest facet size. At 60°C the degree of polarization increased in the order; thiourea>separan>unadulterated>chloride ion. At this temperature, the thiourea-containing solution produced the finest facet size while the chloride ion-containing solution again produced crystals with the largest facet size.

The polarization curves for glue solutions were intermediate to the unadulterated and separan solutions, therefore, the facet size from glue containing solutions was expected to be smaller than those from the unadulterated solutions. However, at both 40 and 60°C the glue solution produced crystals with a larger facet size than the unadulterated solution. Thus, glue-type electrodeposits may be identifiable morphologically, but the polarization curves do not follow the facet size-polarization relationship of the other solutions. Also, these results were produced with one particular glue. There are many varieties of this organic commercially available, each with different chemical and physical properties [15]. Therefore, the results obtained may well depend on the type and specific chemical make-up of the glue used in a particular deposition process.

Deposits made with additive combinations were also examined by scanning electron microscopy to determine which, if either, additive would predominate. A consistent relationship was found at high temperature indicating that the morphology of the copper deposit was related to the polarization curve (Figure 43). The morphologies (Figures 32 to 34) indicate that as the polarization increased the angularity of the facets decreased thereby showing a diminishing effect of the chloride ion upon the morphology.

The electrolyte temperature had a noticeable influence on the morphology of the copper electrodeposits for both single additions and their combinations. These morphological changes were probably due to variations in addition agent activity and stability. Therefore, if this technique were used for electrolyte evaluation, it would be advisable to check the morphology over a range of temperatures. This temperature range should be determined by experimentation so that changes noted in the structure from temperature cycling could be used to indicate additive stability, possible degree of degradition, and possible changes in the relative electrochemical activity of the various additives.

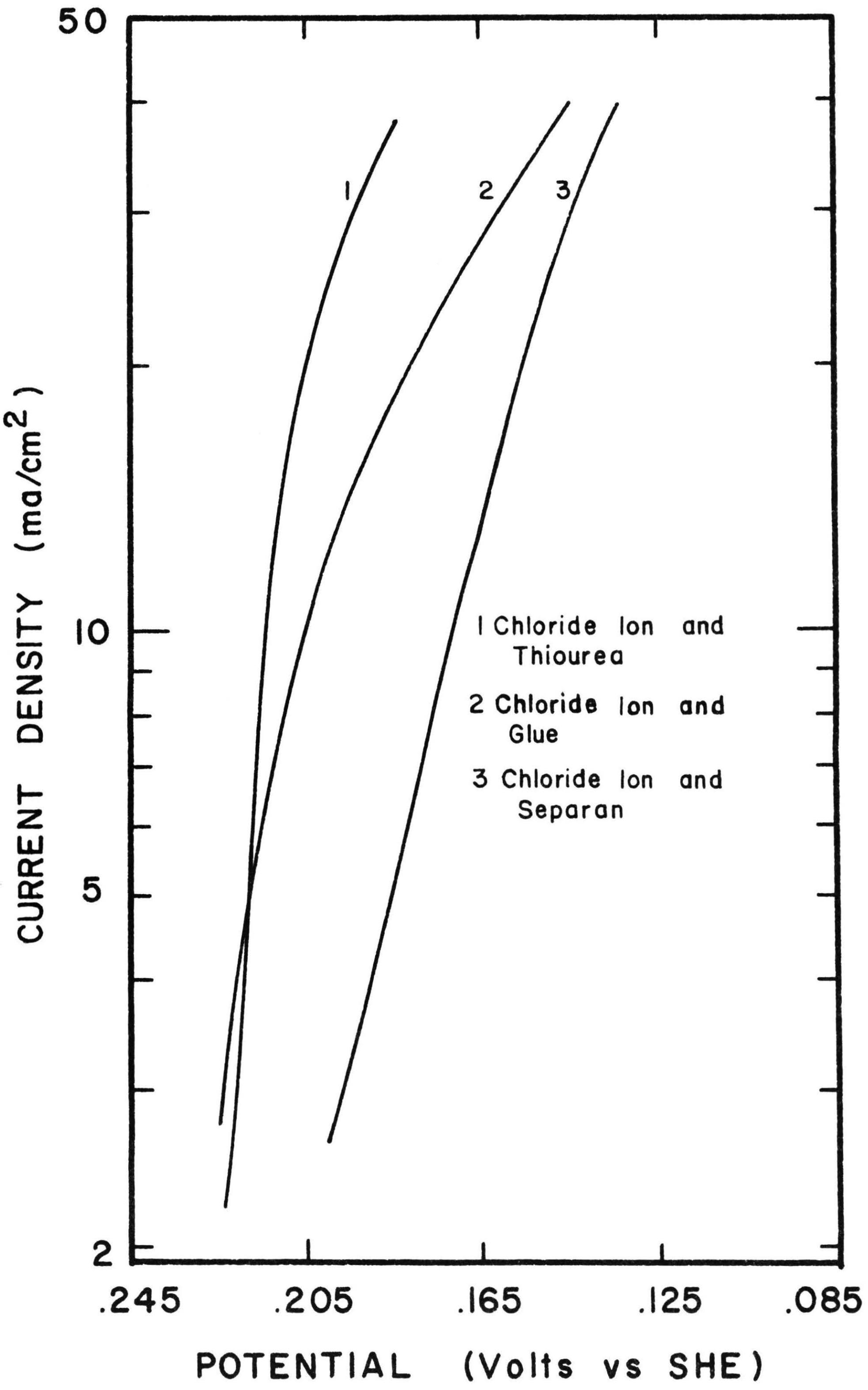

FIGURE 43. CATHODIC SWEEP CURVES FOR ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING TWO ADDITIVES (EACH ADDITIVE AT 50 mg/l). AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

2. Unadulterated, Glue, Separan and Chloride Ion Additions. The cathodic sweeps from the Ti cathode voltammograms produced with the unadulterated, glue-, separan-or chloride ion-containing solutions exhibited a trend between the overall polarization and type of additive. At constant potential, the current densities produced by electrolysis of each solution increased in the order; chloride ion>unadulterated>glue> separan. Thus for these short-time scans the chloride ion acted as a cathode depolarizer whereas the separan acted as a cathode polarizer.

3. Thiourea Additions. The voltammograms from the thiourea-containing solutions showed definitive inflection points, current peaks and current plateaus. These various characteristics were probably due to the interaction of the copper-sulfur film with the metal deposition process. Also, at high electrolyte temperatures it was noted that over a specific range of potential the anodic sweep current densities decreased with increasing thiourea content in the electrolyte. Figures 44 and 45 illustrate this concentration-current density relationship.

The reproducibility of voltammograms generated with the Ti substrate was not as good as those with the Cu substrate. This can most likely be ascribed to a surface oxide film on the Ti cathode. Film characteristics such

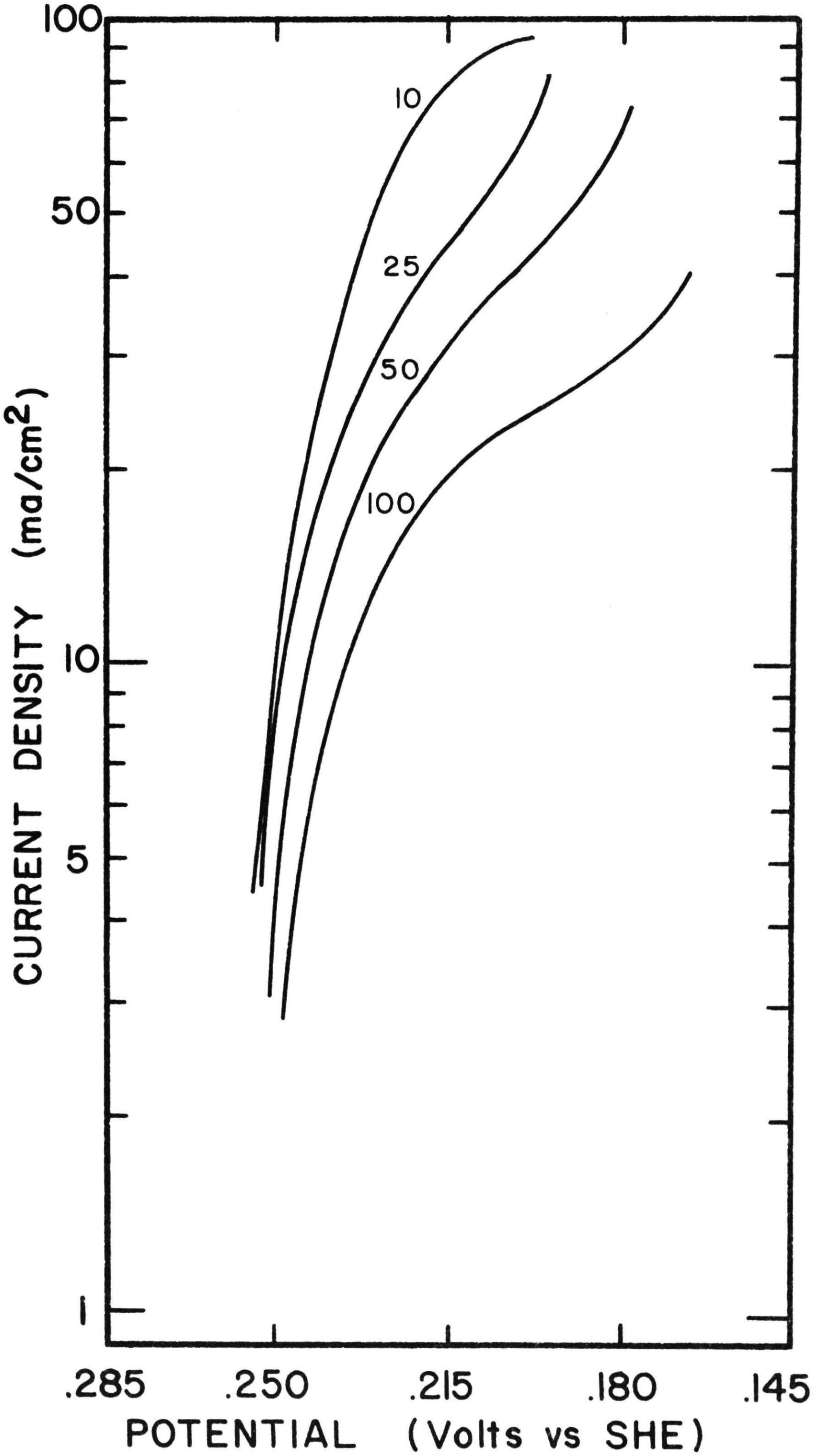

FIGURE 44. ANODIC SWEEP CURVES FOR ACID-SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 50°C CONTAINING 10, 25, 50 OR 100 mg/l THIOUREA. AREA OF TITANIUM CATHODE = 0.5 cm^2.

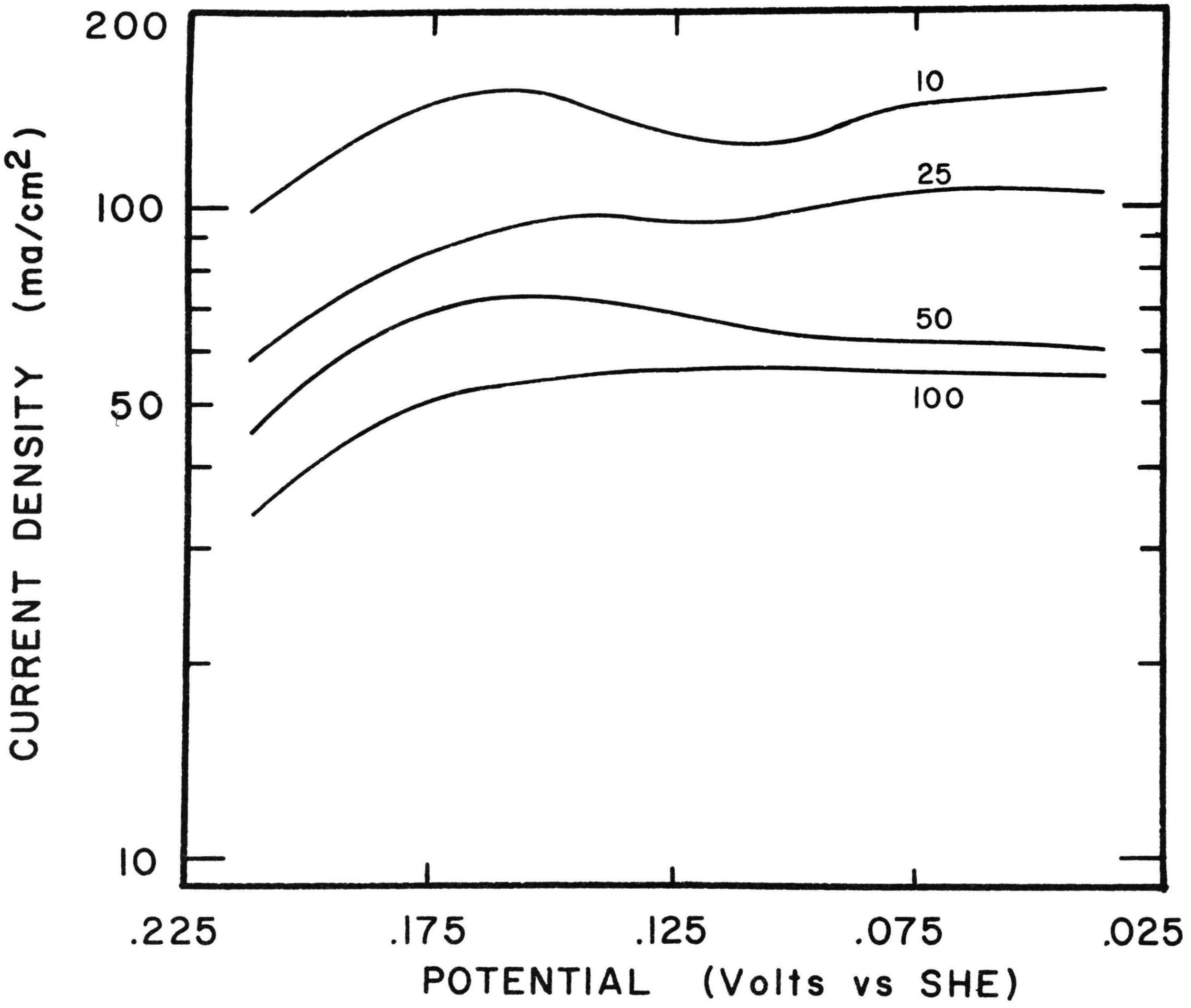

FIGURE 45. ANODIC SWEEP CURVE FOR ACID-SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C CONTAINING 10, 25, 50 OR 100 mg/l THIOUREA. AREA OF TITANIUM CATHODE = 0.5 cm^2. SCAN RATE = 1 mV/sec.

as cathode coverage, overall composition, stability and thickness might not have been consistent for each experimental run thereby resulting in deviations of the polarization behavior.

C. Summary

The experimental results shown indicate the feasibility of using voltammetry and scanning electron microscopy for electrolyte characterization and deposit control. The voltammograms produced from electrolytes using a copper cathode were shown to be a sensitive gauge for detecting the type of addition agent in the electrolyte and also its concentration. The copper electrodeposits produced on the titanium cathode exhibited characteristic morphologies, which could be visually associated with a particular additive in solution. Furthermore, with complex electrolytes, the electrodeposit morphologies can provide information regarding the predominating species in the solution.

D. Titanium Cathode Long-Time Deposits

The long-time copper deposits exhibited surface morphologies which could be associated with a particular additive in the electrolyte. An addition agent's ability to promote leveling on an electrodeposit could be correlated to the deposit's orientation.

1. Deposit Morphologies. The morphologies of the copper deposits from the unadulterated, glue-or separan-containing solutions produced under identical electrolyzing conditions were generally similar. Those from the thiourea-or chloride ion-containing solutions exhibited distinguishably different surface structures. Figures 46 to 51 show SEM photomicrographs of representative electrodeposits produced from these various electrolytes at a temperature of 60°C and a current density of either 20 or 30 amps/ft^2.

The deposits from the unadulterated or glue-containing solutions were nearly identical in overall crystallite size and surface morphology. On each deposit parallel growth steps appeared on the crystal faces. The steps though were more definitive on the deposit from the unadulterated electrolyte. The deposits from the separan-containing solutions had a smaller crystallite size than either deposits from the unadulterated or glue-containing solutions. However, the former deposits did exhibit hemispherical shaped growths on the crystal facets. The occurrence of these growths was enhanced by increasing either the electrolyte temperature or the separan concentration.

Electrodeposits from either the thiourea-or chloride ion-containing electrolytes exhibited surface morphologies which could be visually associated with each particular additive. A characteristic of deposits from the thiourea-

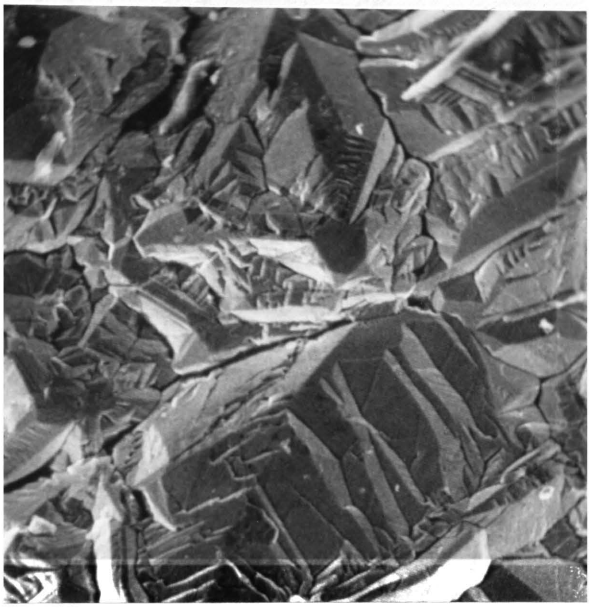

FIGURE 46. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C AND 20 asf. Ti CATHODE. 300x.

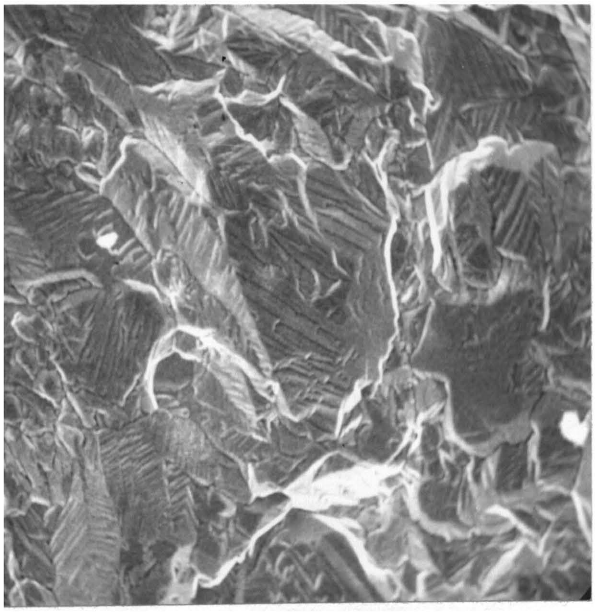

FIGURE 47. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C AND 20 asf CONTAINING 50 mg/l GLUE. Ti CATHODE. 300x.

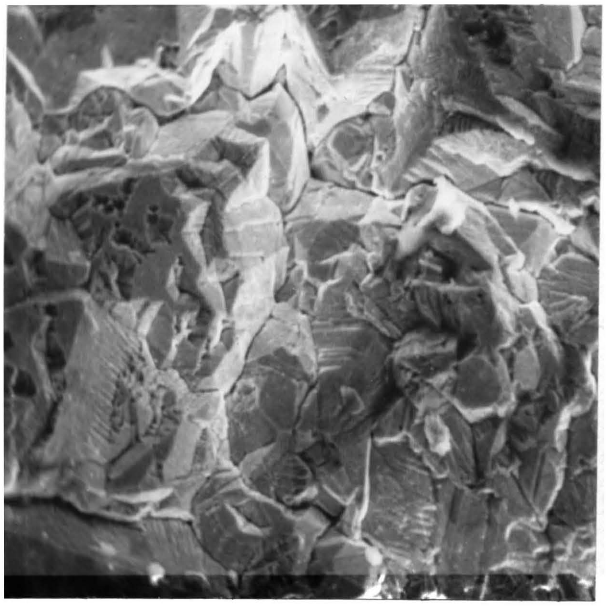

FIGURE 48. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C and 20 asf CONTAINING 0.4 mg/l SEPARAN (DOW NP-10). Ti CATHODE. 300x.

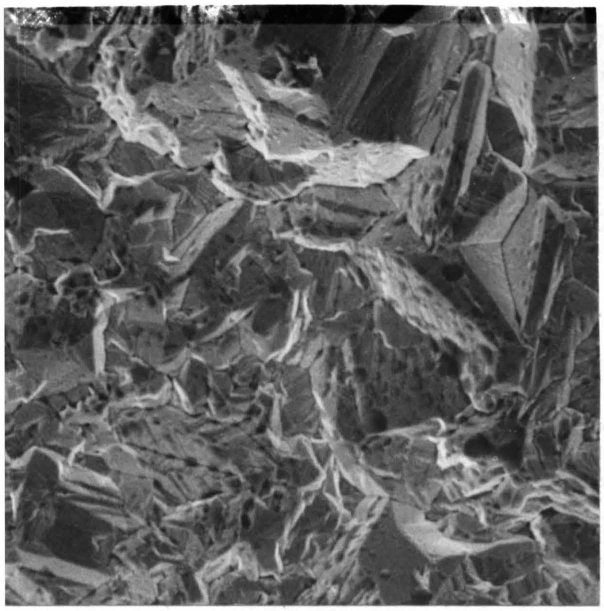

FIGURE 49. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C AND 30 asf CONTAINING 0.8 mg/l SEPARAN (DOW NP-10). Ti CATHODE. 300x.

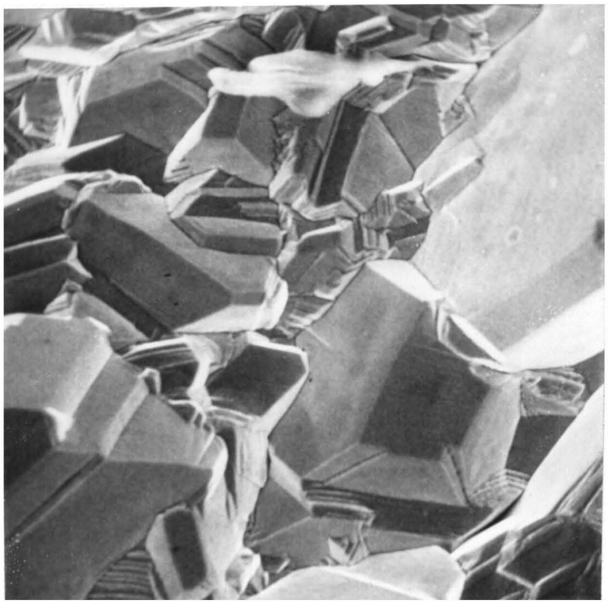

FIGURE 50. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 H_2SO_4) AT 60°C AND 20 asf CONTAINING 0.8 mg/l THIOUREA. Ti CATHODE. 300x.

FIGURE 51. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C AND 20 asf CONTAINING 25 mg/l CHLORIDE ION. Ti CATHODE. 300x.

containing solutions was the predominance of truncated crystals, with cubic and rectangular facets parallel to the electrode surface. Preferential pitting on certain crystal faces was a noticeable characteristic of deposits from an electrolyte containing the chloride ion. The pits were small in size and their occurrence was enhanced by increasing either the electrolyte temperature or chloride ion concentration. However, increasing the current density diminished the pitting effect.

The various additives also imparted other characteristics which affected the surface morphology and growth mode of the copper electrodeposits. The chloride ion promoted outward growth of the initial copper nuclei at high electrolyte temperature and high chloride ion concentration. This outward growth was detrimental in that it decreased the adhesion between the copper deposit and Ti substrate. With high electrolyte temperature, high chloride ion concentration and low current density, the copper deposits were incomplete or "lacy". Figure 52 shows a typical "lacy" deposit. The cause of these incomplete deposits might be attributed to film formation on the Ti cathode. The chloride ion could possibly interact on the cathode surface during the onset of electrolysis, forming a film on certain portions of the cathode, thereby rendering these portions unsuitable for metal deposition. Furthermore, once this condition is initiated it cannot

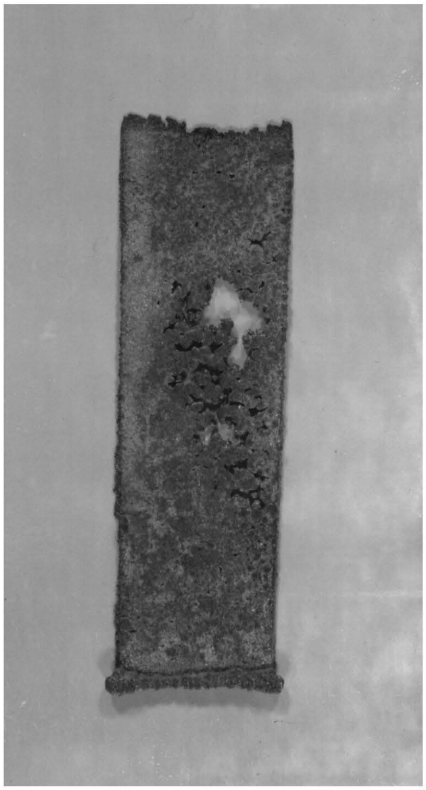

FIGURE 52. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 60°C AND 10 asf CONTAINING 25 mg/l CHLORIDE ION. Ti CATHODE.

be rectified without physically or chemically treating the cathode. The needlelike crystals, which were observed from the chloride ion-containing electrolyte in the short time scans were also observed in the long time deposits, (Figure 53).

The effects of high electrolyte concentrations of thiourea (100 mg/l) or separan (50 mg/l) were investigated. These two addition agents produced brittle deposits and growth was susceptible to the electrolyte flow pattern. This gave deposits with an uneven surface containing nodular dendritic crystals interspersed throughout the deposit. The brittleness of the deposit from the thiourea-containing electrolyte could have been due to thiourea or some of its components being incorporated into the deposit, as sulfur has been found in electrodeposits produced from thiourea-containing electrolytes [3].

Figure 54 shows quite vividly the characteristic truncated crystals produced by a thiourea-containing electrolyte.

2. Deposit Orientations. Electrodeposits from the unadulterated or chloride ion-containing solutions exhibited predominantly (220) orientations, but the (111) peak intensities were lower with the deposits from the unadulterated electrolyte. The deposits shown in Figures 46, 51 and 53 were all (220) oriented. Solutions

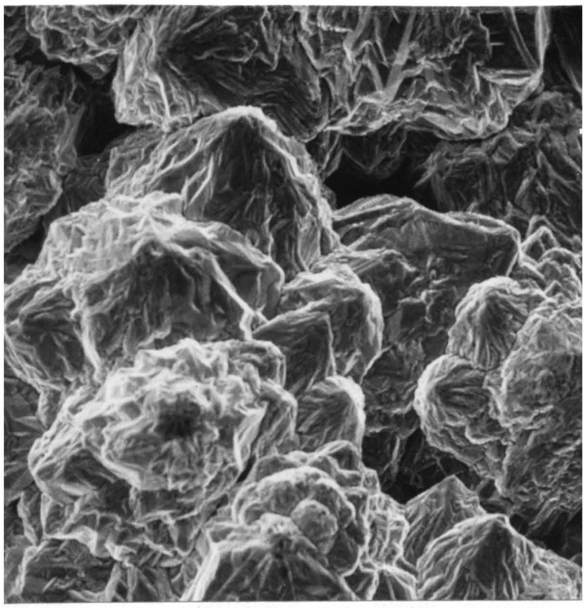

FIGURE 53. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 30 °C AND 40 asf CONTAINING 25 mg/l CHLORIDE ION. Ti CATHODE. 300x.

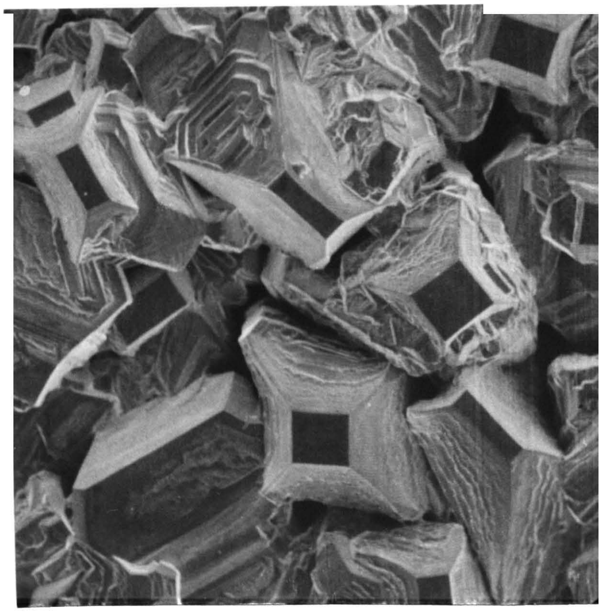

FIGURE 54. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED COPPER SULFATE ELECTROLYTE (45 gpl Cu^{++}, 200 gpl H_2SO_4) AT 40°C AND 30 asf CONTAINING 0.4 mg/l THIOUREA. Ti CATHODE. 300x

containing 25 mg/l glue produced deposits that showed a random* type of orientation, however the (200) and (220) peak intensities were slightly more intense than those for a perfectly random copper deposit. Deposits from electrolytes containing 50 mg/l glue showed that upon increasing the electrolyte temperature, the orientation shifted from a random type to a (220) type. Figure 47 shows a (220) orientation. The orientation produced from solutions containing low concentrations of separan (.4 and .8 mg/l) was (220). Solutions containing 50 mg/l separan produced deposits whose orientation was either (111) or (200). The truncated crystals from the thiourea-containing solutions exhibited a (200) orientation (Figure 54), while the other types of morphologies showed either (111) or (220) orientations.

A level electrodeposit resulted when its orientation was (220). Shifts in the orientation from (220) to either (200) or (111) resulted in physically rougher deposits, with the deposits oriented (111) showing the greatest degree of surface roughness.

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*In a perfectly random copper deposit, the intensity of the (111) peak is 100, while the intensities of the (200) and (220) peaks are 46 and 20 respectively.

V. CONCLUSIONS

(1) The combination of voltammerty and scanning electron microscopy could be used as a technique to evaluate the electrolyzability of commercial electrorefining or electrowinning solutions.

(2) Correlations exist between the voltammograms and short time electrodeposit morphologies which would allow characterization of the type and the concentration of an addition agent.

(3) Characteristic and reproducible voltammogram features (e.g. current peaks, limiting current plateaus, etc.) were exhibited with certain additives.

(4) The polarization behavior and short time crystal morphologies were dependent upon cathode substrate, type and concentration of additive and electrolyte temperature.

(5) Synergistic effects, as well as the predominating additive in electrolytes containing several addition agents, could be determined by examination of the short time crystal morphologies.

(6) Variations in the crystallization behavior and orientations of the long time deposits were noted with changes in the current density and electrolyte temperature.

(7) The long-time copper deposits, under certain deposition conditions exhibited crystal morphologies (e.g. truncated crystals, pitting, etc.) characteristic of the additive in solution.

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APPENDIX A

GALVANOSTATIC COPPER DEPOSITION ON Ti CATHODES

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GALVANOSTATIC COPPER DEPOSITION ON Ti CATHODES

Galvanostatic experiments were conducted using either a Sorenson QRC 40-15A or a Hewlett-Packard 628A DC power supply in a two liter, pyrex tank, 7.5" x 5" x 4". A 0.25" thick plexigalss top was machined as a cover and electrode spacer for the electrolytic cell. Two electrowon copper sheets, 4.5" x 2" x 0.125", were used as the anodes and one titanium sheet, 5" x 1" x 0.05", was used as the cathode. The titanium cathode was placed in the center of the pyrex cell with a copper anode on either side, spaced 1.5" from the Ti cathode. Banana plugs were mounted onto the plexigalss holder thereby supporting the electrodes and providing electrical contact. Teflon edge strips were placed on the edges of the Ti cathode to eliminate current concentration and block dendritic growth. Prior to immersion into the electrolyte the titanium cathode was etched in a solution of 2.5 vol.% HNO_3, balance H_2O. The etched cathode was washed with distilled water, rinsed with acetone and dried in an air stream. The copper anodes were pretreated in an identical manner as the titanium cathode except that the etching solution was 40 vol.% HNO_3, balance H_2O.

A 1N H_2SO_4 salt bridge with a Luggin capilary and a Keithley 610C electrometer were utilized to measure cathodic polarization during an experimental run. The reference electrode was Hg/Hg_2SO_4 (1N H_2SO_4). The potential was continuously monitored and also recorded onto an Esterline Angus strip chart recorder.

The cleaned and dried cell was filled with the proper amount of electrolyte, covered, and placed in a Precision Scientific Lo-Temp circulating system and allowed to stabilize to the required temperature. When the proper temperature was attained the electrodes were placed into the cell and electrolysis begun.

The duration of electrolysis was varied, depending on the applied current density, to give a 24 gram copper deposit. At the conclusion of electrolysis the titanium cathode was removed from the plexigalss cover, washed with distilled water, rinsed with acetone and dried in an air stream. The electrodeposited copper was removed from the cathode by flexing and the copper deposit was again washed, rinsed and dried.

VITA

Louis Francis Toth, Jr. was born on November 27, 1947, in Elizabeth, New Jersey. He received his primary and secondary education in Carteret, New Jersey. He received a Bachelor of Science degree in Metallurgical Engineering from the University of Missouri-Rolla, Rolla, Missouri, in January, 1970.

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