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THE EFFECT OF AN ORGANIC ADDITION AGENT ON CUPRIC FLUOBORATE ELECTRODEPOSITS

by

Philip Morrison Baird

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Metallurgy and Materials Science

Lehigh University

1973

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

13th April 1973
Date

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ABSTRACT

The effects of a proprietary organic addition agent (Cubath Hy, Sel Rex Co.) on electrodeposits from a cupric fluoborate electroplating bath have been studied. A number of physical and mechanical properties of the deposit were found to correlate with addition agent concentration. At additive concentrations of 5 ml/l to 15 ml/l a deposit was produced with a surface roughness of less than 20 μ-in, a resistivity of about 1.8 $\mu\Omega$-cm, a ductility as percent elongation of ~12%, and a tensile strength of 42 to 47 kpsi. A change in microstructure from columnar to fine occurred in the 1/2 - 4 ml/l concentration range. Surface morphology was observed to change with microstructure. Fracture surface morphology under tensile loading followed changes in microstructures and ductility. Plating efficiency decreased with increasing additive concentration.

The use of the organic addition agent in the cupric fluoborate electroplating bath was found to provide deposits which are suited for printed wiring board and other applications at a significantly improved plating rate.

I. INTRODUCTION

In the manufacture of communications equipment, electroplating is widely employed for wear and corrosion resistance, and also to form conductive layers on dielectric printed circuit materials.

Printed wiring boards are finding increasing use as interconnection devices in communications equipment. A printed wiring board is an electrically conductive pattern bonded to a dielectric material, which may be either rigid or flexible.[1] For many double-sided and multilayer printed wiring boards, electroplating is used to rapidly build up conductor paths in drilled and chemically metallized through holes for side-to-side or interplane connections.

Recent additive techniques for manufacturing printed wiring boards provide an economic advantage over currently employed subtractive methods but also place increased reliance on electroplating. Conductor paths, which would ordinarily be formed by etching away unwanted laminated copper foil, are formed along with the interplane through hole hole connections by initial electroless chemical metallization followed by full electroplating.

Most electroplating technology applied to printed wiring boards has been extended from metal finishing techniques for producing decorative and protective surfaces. For copper plating, acceptable product has been obtained using a copper sulfate bath and organic addition agents. However, the maximum plating rate for acceptable product has remained low in comparison with other baths. In most cases printed wiring boards which were plated in fast baths failed to meet one or

more of the essential requirements for surface roughness, conductivity, ductility, and strength.

Along with the continuing need to meet product requirements for leveling or surface roughness, conductivity, ductility, and strength, the economics of electroplating has become of increasing importance.

Copper plating baths using a cupric fluoborate electrolyte are reported to exhibit the highest plating rates because of the high solubility of the copper ion in fluoborate.[1-6] There exists some evidence to show that the use of organic addition agents with $Cu(BF_4)_2$ will produce level and ductile deposits at high deposition rates.[7-14]

Evidence for level and ductile plating is generally qualitative. Plating systems have been studied in relation to specific properties. Quantitative data is often absent, especially for leveling. Current densities and temperatures chosen for investigation vary widely and prevent correlation of data from different sources.

C. J. Milora[8] employed a groove test and reported a leveling value of 0.85 (on a scale with 1.0 as complete leveling) for a pure $Cu(BF_4)_2$ system and a value of 1.0 using Cubath Hy, a proprietary addition agent by the Sel Rex Co., Nutley, New Jersey. Toledo[14] reported bright and level deposits at high current densities using a proprietary addition agent, UBAC #1,* in conjunction with a small amount of sulfate ions. Patents by Creutz, et al[11,12] and Brugger[13] presented addition agents for cupric fluoborate which it is claimed produce leveling and ductile copper.

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*Udylite Corp., Detroit, Michigan.

These patents do not report any quantitative values. Many investigators[2,7,15,16] have reported the non-additive fluoborate bath to produce a "smooth" deposit.

Resistivity values for non-additive $Cu(BF_4)_2$ deposits have been measured and values of 1.73-1.75 microohm-cm are typical.[4,15] Ductility as measured by percent elongation over a 2 inch gage length has been reported in the 3.2 to 41% range[2,4,15] over a current density range of 15-300 amperes per square foot (asf). Henrickson[3] reported 1.9-4.8% elongation and tensile strengths of 41 to 59 kpsi testing thin foils produced at 120-240 asf. Tensile strength was reported by Struyk and Carlson[2] to be 17.1 to 32.5 kpsi, utilizing a current density of 300 asf. Other investigators[4,10,15,16] have reported tensile strengths of 17.1 to 38 kpsi.

The question arises as to whether the leveling, electrical, and mechanical properties of a plating system can be explained in terms of physical properties.

The term leveling is used to describe the smoothing of a surface by an applied deposit. This may occur on either a microscopic or a macroscopic scale. There are two types of leveling. Geometric leveling is the result of grain growth perpendicular to the substrate surface. When two growing surfaces meet in a recess and fill it, geometric leveling has occurred.[17] The second type is electrochemical leveling. Deposition preferentially occurs in the recesses of the substrate surface. The two cases are not mutually exclusive and may simultaneously occur in some cases.

In order to produce leveling some plating solutions require the addition of an organic agent in small quantities. This addition agent is incorporated into the deposit.[17,19-23] In a radioisotopic study of leveling in a nickel bath, Beacom and Riley[22] showed the addition agent to be preferentially deposited at the high points of an irregular surface. Two theories have been proposed to explain how preferential deposition may cause leveling. One hypothesis suggests that leveling is caused by differential diffusion rates set up by local concentrations of the addition agent. The second hypothesis proposes that the adsorbed additive leads to localized polarization. Consequently deposition at the peaks is inhibited and electroplating current is diverted to the hollows.[19-21] A number of investigators[17,19-23] have shown that leveling agents increase cathode polarization.

Henrickson[3] found that the electrical resistivity of the deposit was a function of the internal stress of the deposit. He found that the resistivity of the electrodeposited copper dropped to approximately bulk value after annealing.

Deposits from cupric fluoborate baths have been most frequently reported to exhibit a columnar microstructure.[3,15] Other investigators have reported a columnar to fibrous structure.[4,16] Saubestre and Khera[9] presented a micrograph of a fine structure from a deposit produced with a proprietary brightening system, Enthobrite* Cu-942, M, R, & S.

*Enthone, Inc., West Haven, Connecticut.

Although the literature discusses deposit properties, information is generally qualitative rather than quantitative. For use with printed wiring board plating, comprehensive and quantitative data on a plating system is essential.

The purpose of this work is to provide useful quantitative data for a plating system which will meet minimum requirements of leveling, ductility, conductivity, and plating rate.

A cupric fluoborate electrolyte with Cubath Hy as an addition agent was chosen for study based upon the earlier work of Milora[8], who showed Cubath Hy in $Cu(BF_4)_2$ to produce a level deposit. The maximum acceptable surface roughness was 20 microinches, center line average. A minimum elongation of 3% in a 2 inch gage length was required. A current density of 150 asf was chosen as a minimum economic current density. Early experiments and manufacturer's recommendation lead to selection of a 25-26°C temperature control point with individual baths being regulated to ±1/2°C of the set point. The investigation will explore the leveling ability of the plating system, the electrical and mechanical properties, and changes in the above properties in relation to physical properties of the deposit.

II. CAN LEVELING BE ACHIEVED

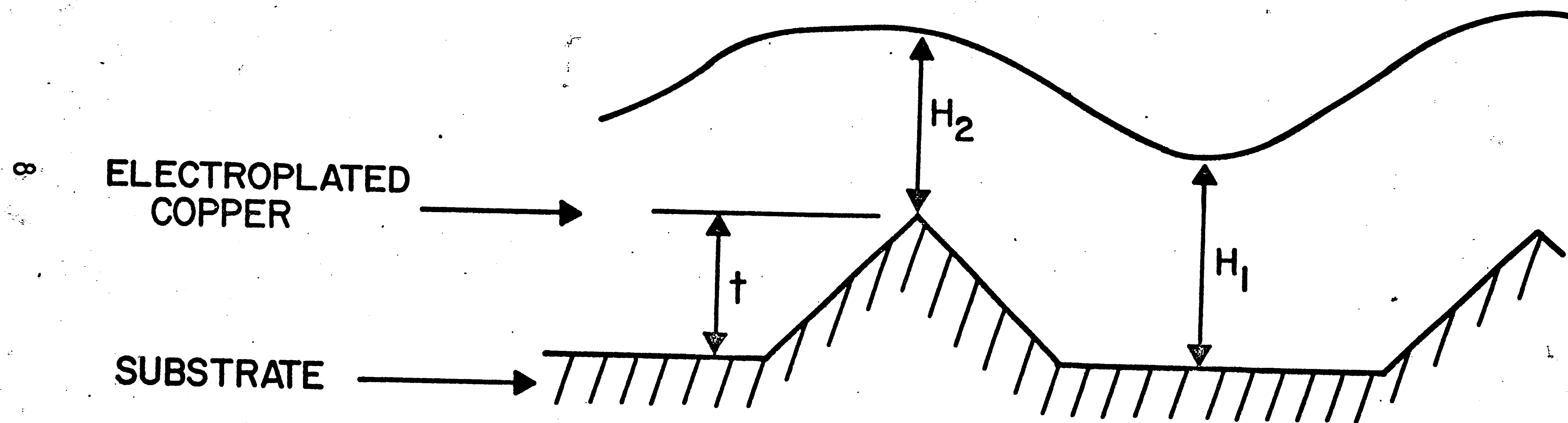
The ability of a plating system to smooth a rough surface, to level, is in many applications a highly desired property. Cubath Hy in copper fluoborate is reported to possess such a property. [8] To verify this report and establish the parameters necessary to achieve leveling, the microleveling and macroleveling properties were investigated.

Microleveling, in this usage, is the inherent ability of the bath to smooth a rough surface by preferential deposition. To test this property a standard rough surface, a male record stamper, was chosen. A record stamper is the die used to make phonograph records. It produced a surface with evenly spaced lands separated by ridges of uniform height. Samples were plated on this surface. Microleveling was evaluated using the following quantitative scheme.

$$E = \frac{H_1 - H_2}{t} \cdot 100\%$$

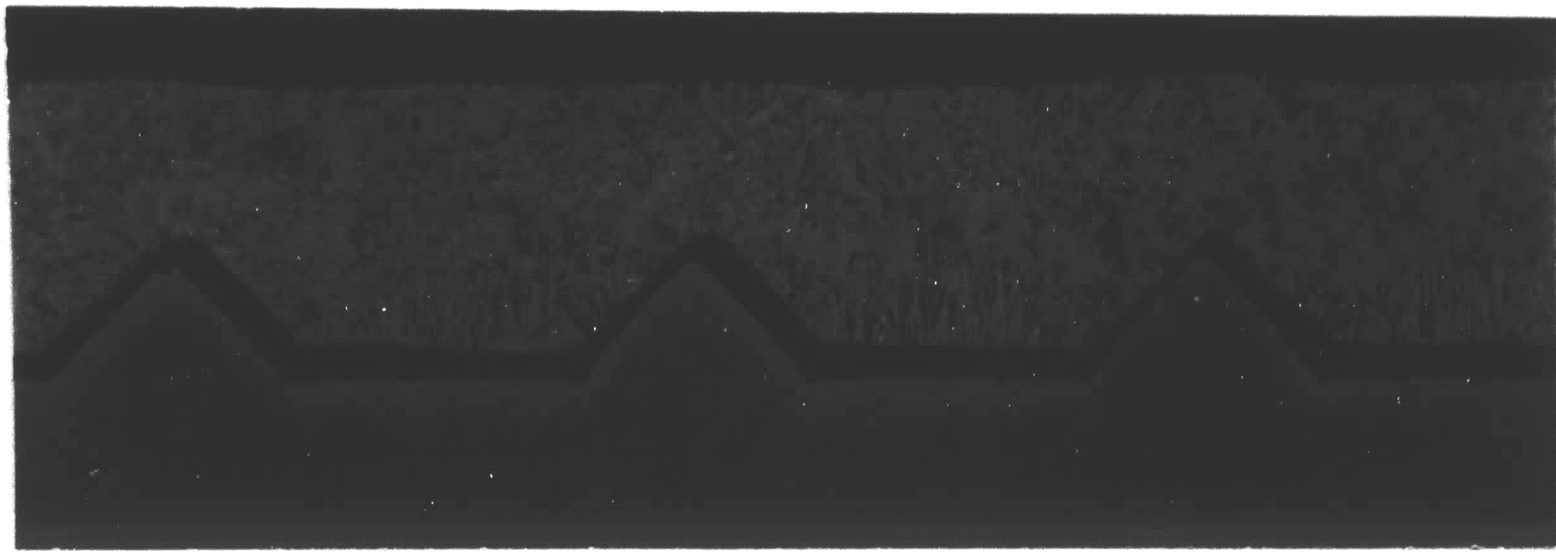
E is the microleveling ability in percent, H_1 is the plating height over the land, H_2 the deposit height over the ridge, and t is the ridge height (see Figure 1). With this scheme perfect leveling gives a value of 100%, partial leveling produces a value greater than zero, and a negative number represents increased roughness. For the anomalous case where the plating thickness over the land was thicker than the plating over the ridge (see Figure 2), the value was symmetrically inverted to show a partial or negative leveling value by use of the equation.

CALCULATION FOR MICROLEVELING



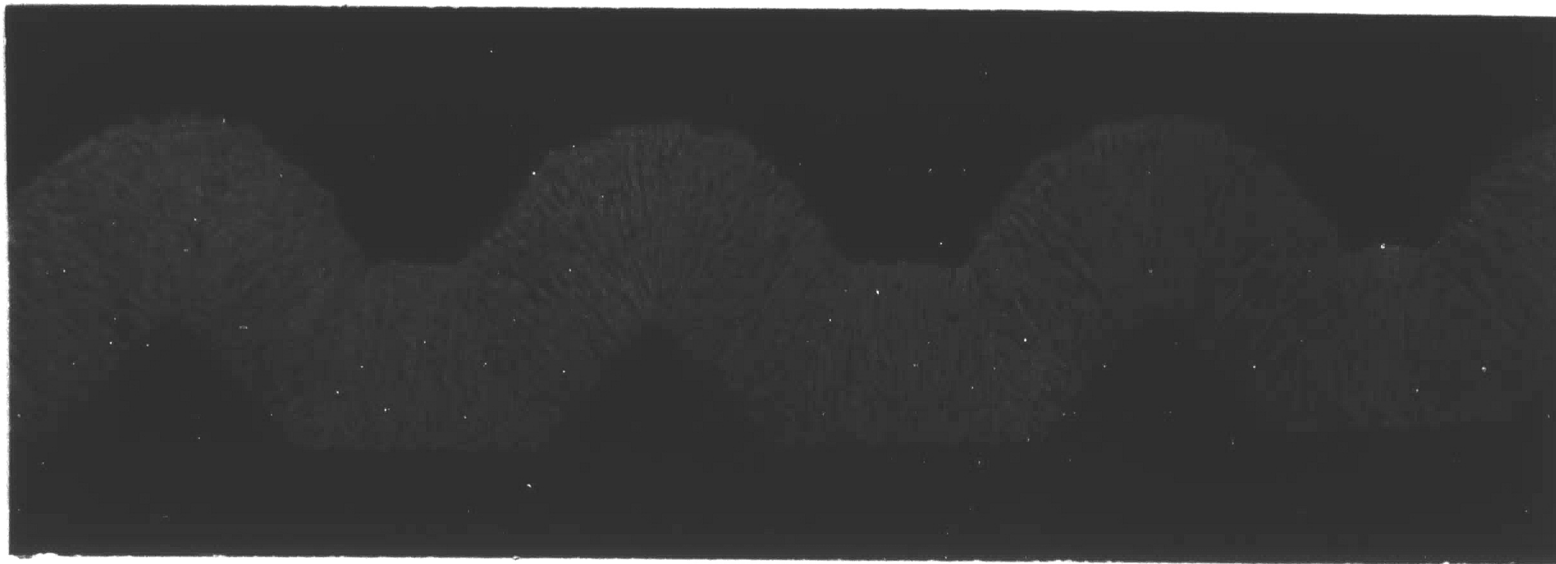
$$E = \frac{H_1 - H_2}{t} \cdot 100\%$$

FIGURE I.



200X

A. PERFECT LEVELING



200X

B. PARTIAL LEVELING

100X

C. PARTIAL LEVELING -
ANOMALOUS CASE

FIGURE 2. PHOTOMICROGRAPHIC CROSS-SECTIONAL VIEW OF MICROLEVELING ABILITY

$$E^* = 1 - (E - 1)$$

where E* is the inverted value and E the initial value over 100%.

Figure 3 is the graph of microleveling ability versus additive concentration. The line is drawn to indicate the trend of the data. The $Cu(BF_4)_2$ bath without additive produced a deposit with increased roughness (a negative microleveling value). With the addition of small amounts of Cubath Hy the microleveling is quite good, but gradually decreases with further increasing concentrations of Cubath Hy. It should be noted that these were small scale samples and were not produced in the same apparatus as was used for subsequent large scale samples. Variations in system performance will be discussed in section IV.

Macroleveling, as surface roughness, was determined by the center line average roughness as measured by a Talysurf 4.* Surface roughness was plotted against additive concentration in Figure 4. The line was drawn to point out the general trend of the data. From an initial average value of 75 microinches with no additive, the trend is decreasing surface roughness with increasing additive concentration. It should be noted that a large amount of scatter is observed in the 1-4 ml/l concentration range. This scatter and other aspects of the 1-4 ml/l range will be discussed in sections IV and V. At 5 ml/l and greater the scatter is small and roughness gradually decreases with increasing Cubath Hy concentration. Beyond 5 ml/l additive the average surface roughness drops below 20 μ-in, the condition it was

*Taylor-Hobson, by Engis Equipment Co., Morton Grove, Illinois.

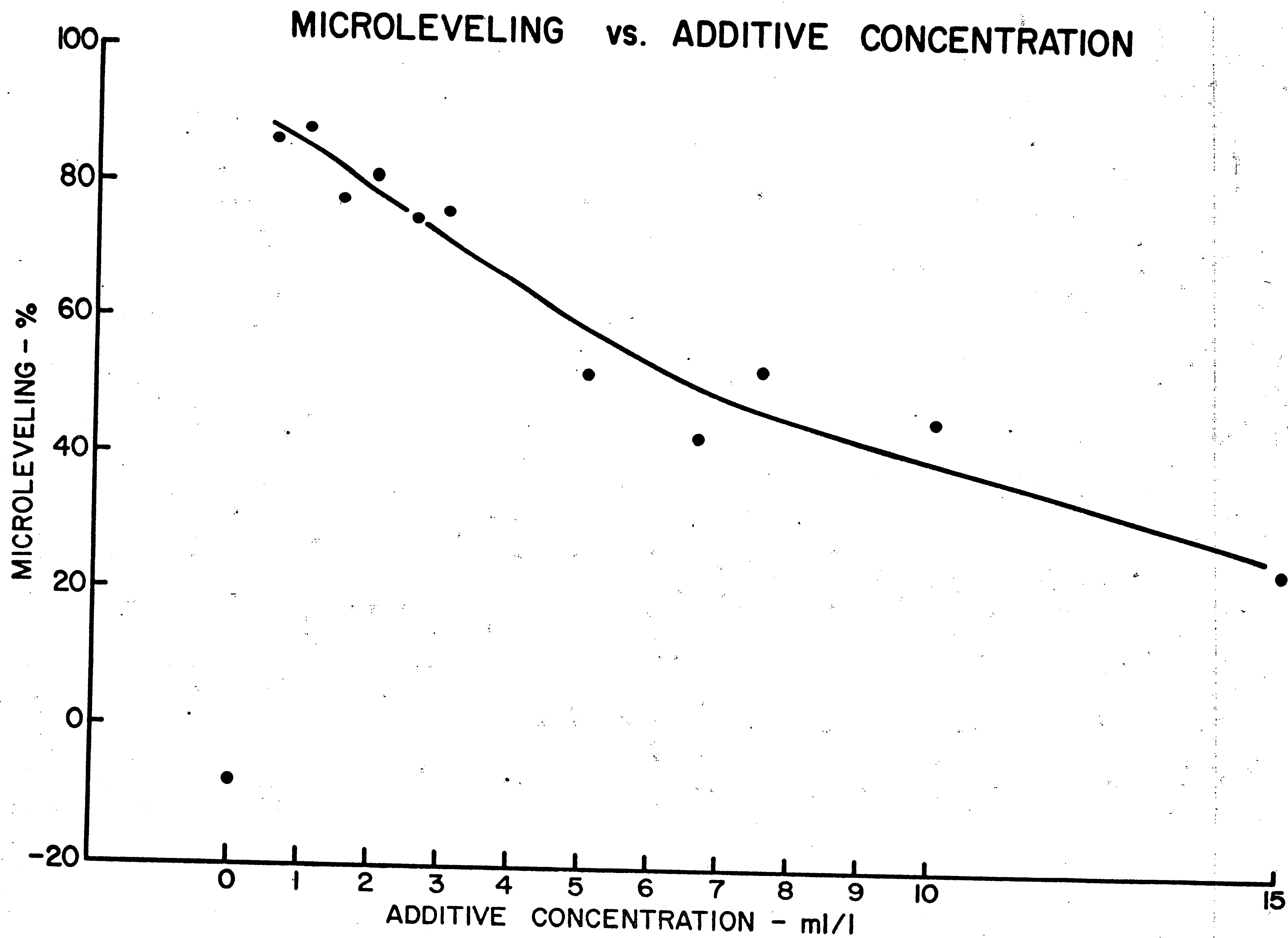


FIGURE 3.

SURFACE ROUGHNESS vs. ADDITIVE CONCENTRATION

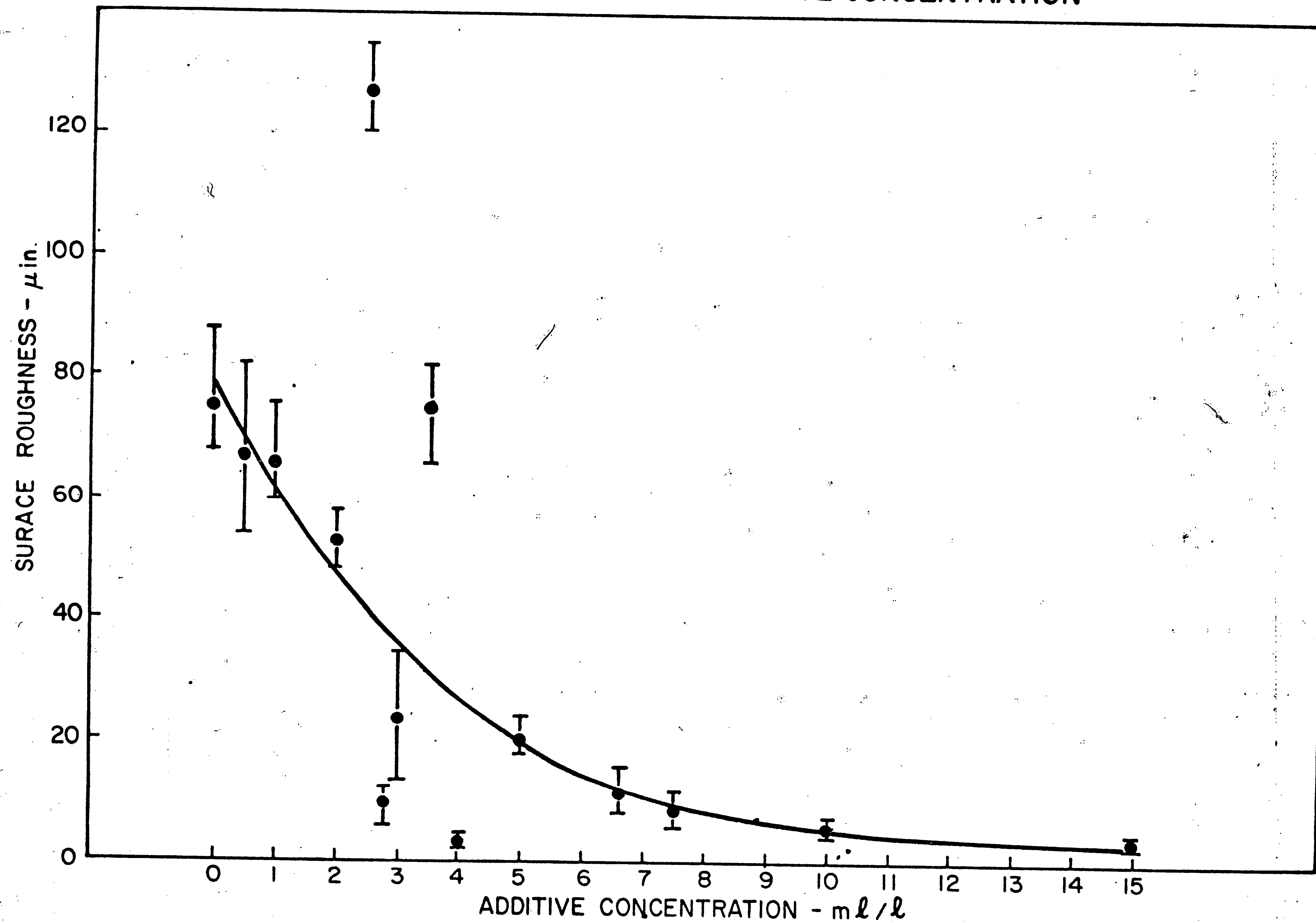


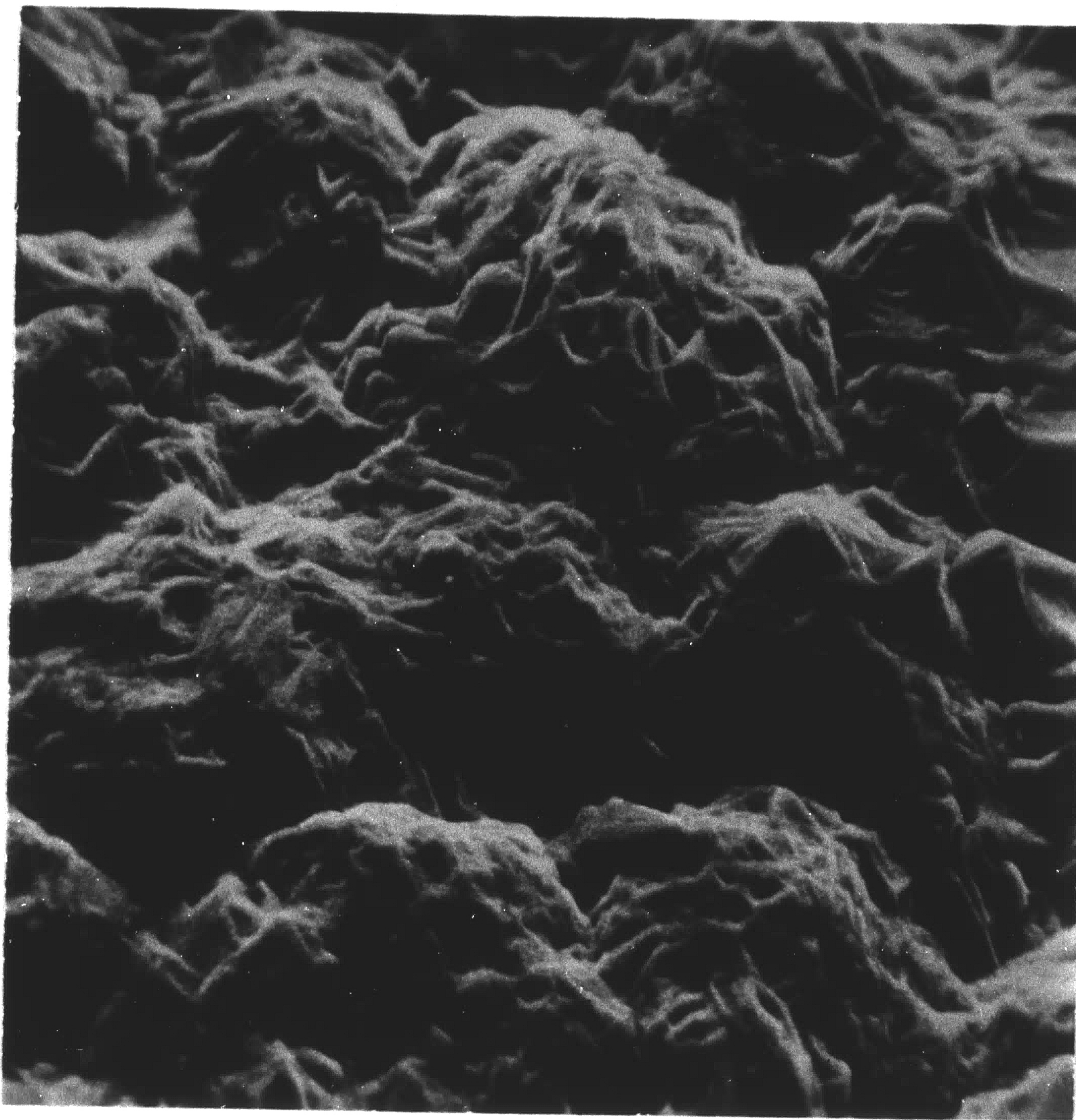
FIGURE 4

desired to achieve.

To further study the surface morphology scanning electro micrographs were taken. A representative surface micrograph of a deposit from the non-additive $Cu(BF_4)_2$ bath is shown in Figure 5a. When Cubath Hy in concentrations of 1/2 ml/l to 2 ml/l is added, a typical surface structure is shown by Figure 5b. The change in morphology is very distinct. With this small amount of additive the surface is rough in gross detail, but the individual features soften and blend into the gross detail. With the increase in additive concentration to 2.5 ml/l and greater, a dramatic change in the surface takes place. Figure 5c is typical of the surface in this concentration range. At 2500X no details of the surface structure are evident. Micrographs taken at 12,500X also failed to resolve any surface detail. In this concentration range, and especially above 4 ml/l, the surface of the deposits was specular.

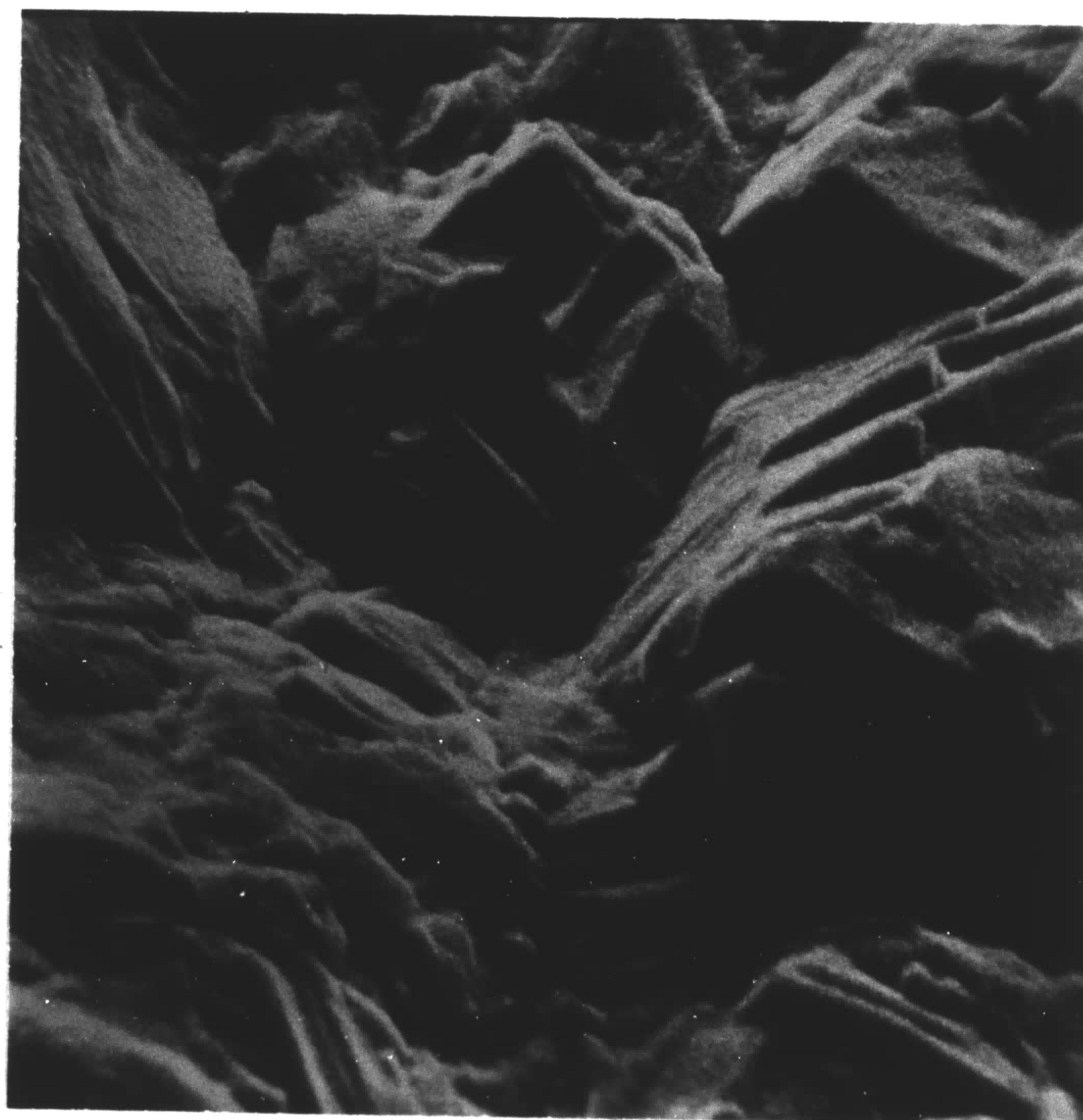
From the above, several observations come forth. Cubath Hy in a $Cu(BF_4)_2$ electrolyte is capable of producing a deposit which exhibits both microleveling and macroleveling properties. The amount of leveling is dependent upon the additive concentration, and a distinct change in surface morphology occurs above a Cubath Hy concentration of 2.5 ml/l.

To determine the effect of the Cubath Hy addition agent on deposition rate, a relative plating efficiency was determined by normalizing the deposit thickness from each Cubath Hy concentration with the thickness of the non-additive deposit. Plating efficiency



2500X

A. NO ADDITIVE



2500X

B. LOW ADDITIVE CONCENTRATION, 1/2 - 2 ML/L

FIGURE 5. SCANNING ELECTRON MICROGRAPHS OF DEPOSIT SURFACE MORPHOLOGY

2500X

C. ADDITIVE CONCENTRATION GREATER THAN 2.5 ML/L

FIGURE 5 CONTINUED

was plotted as a function of additive concentration in Figure 6. The line was drawn to indicate the trend of the data. The plating efficiency decreased with increasing additive concentration.

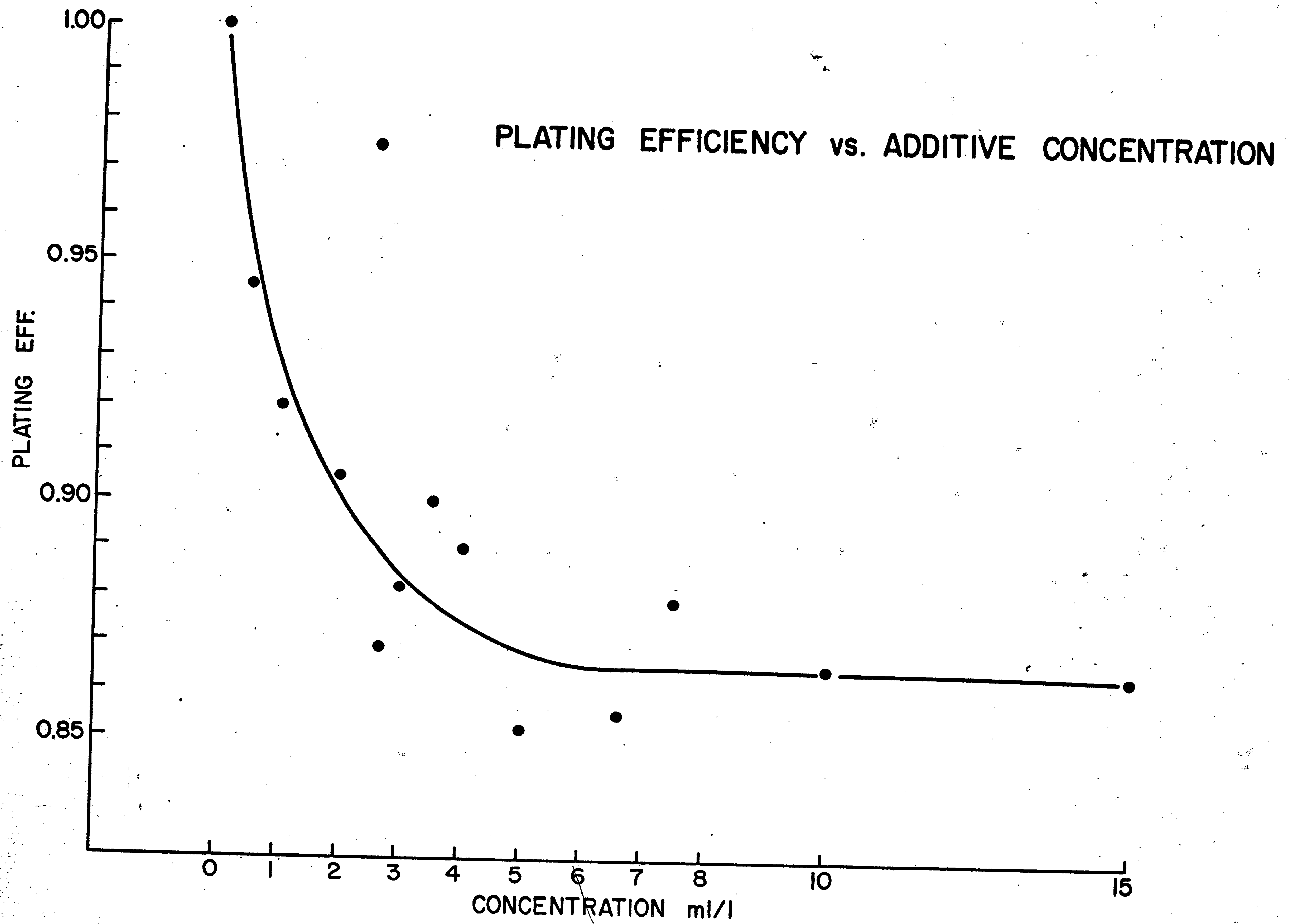


FIGURE 6.

III. THE PRICE OF LEVELING

Initially, it was determined that a cupric fluoborate bath with a suitable concentration of Cubath Hy as an additive will provide suitable leveling. For many applications, such as printed circuits, it is essential to determine the effects of the addition agent on critical mechanical and electrical properties.

Tensile tests were performed to measure tensile strength and ductility as determined by percent elongation to failure. Figure 7 is the plot of tensile strength versus additive concentration. A curve is drawn to indicate the general trend of the data. The mean value of the data is shown by dots, and the bands depict the full range of the data. The average tensile strength of a sample plated in the standard bath with no additive was 43 kpsi. With addition of Cubath Hy, the tensile strength initially dropped. The scatter in the data showed a significant increase. Scatter was at a maximum between 1/2 ml/l and 2 ml/l of additive. At a Cubath Hy concentration of 5 ml/l, tensile strength values approached the values of the non-additive bath. Increasing additive concentration beyond this point caused a trend of increasing tensile strength, reaching an observed maximum of 47 kpsi at a Cubath Hy concentration of 15 ml/l.

Figure 8 shows per cent elongation as a function of additive concentration. From an initial average value of 15%, percent elongation at failure (which will be used interchangeably with ductility) decreased as initial small amounts of Cubath Hy were added to the bath. With increasing additive concentration copper ductility

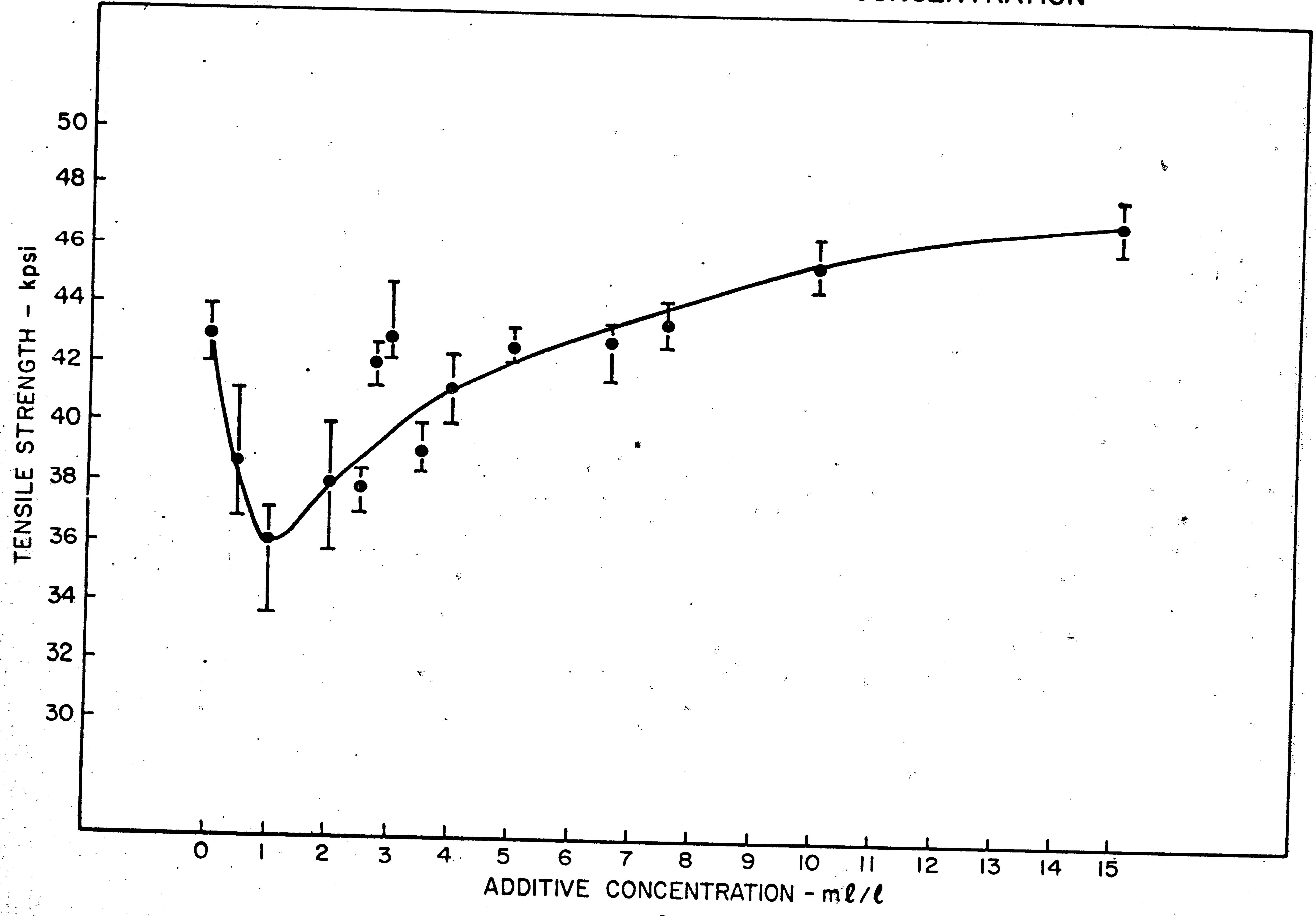


FIGURE 7.

ELONGATION vs. ADDITIVE CONCENTRATION

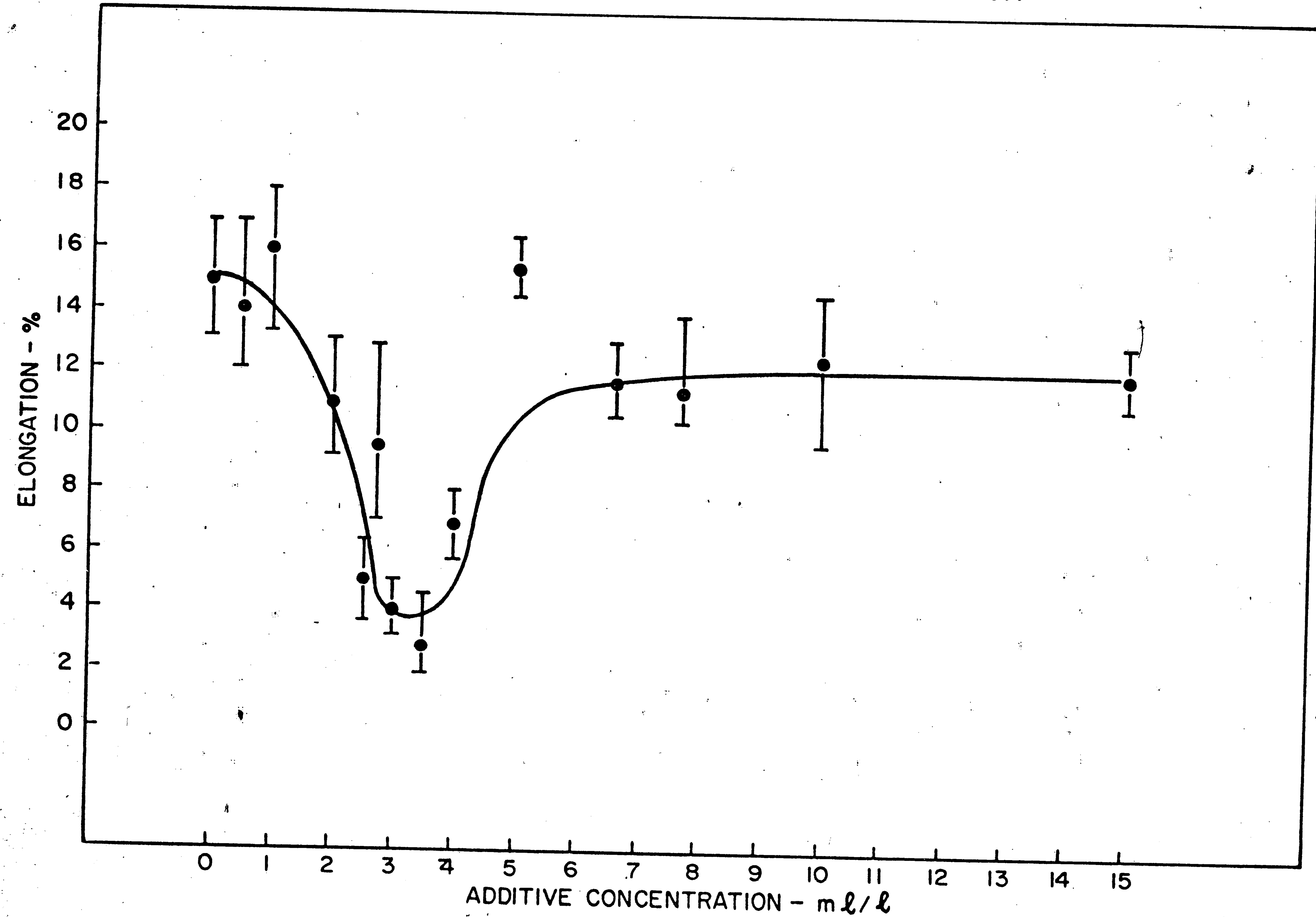


FIGURE 8.

appeared to go through a minimum and then recover. Again it must be noted that the curve is intended to indicate the general trend of the data. Note that recovery of ductility has occurred beginning with an additive concentration of 5 ml/l. Above this concentration the average ductility remains fairly constant.

The resistance of the deposited samples was measured so that resistivity in units of microohm centimeters could be calculated using the following equation

$$\rho = \frac{RA}{L}$$

Resistivity has been plotted in Figure 9 as a function of additive concentration. At low concentrations, no correlation was observed. It is interesting to note the wide fluctuations in strength and ductility also observed in this additive concentration range. However, around a concentration of 5 ml/l the resistivity values appeared to stabilize and a curve has been drawn to indicate this trend. This data was repeatable within 2 1/2%.

It should be noted that in each of the three figures presented, the properties as plotted versus concentration exhibit a recovery or stability at additive concentrations of 5 ml/l and above. The tensile strength of the additive deposit approaches the strength of the non-additive deposit at 5 ml/l and was greater than the non-additive deposit strength when additive concentration was greater than 5 ml/l. Percent elongation reached a value of 12% at concentrations above 5 ml/l. Variations were small. At additive concentrations

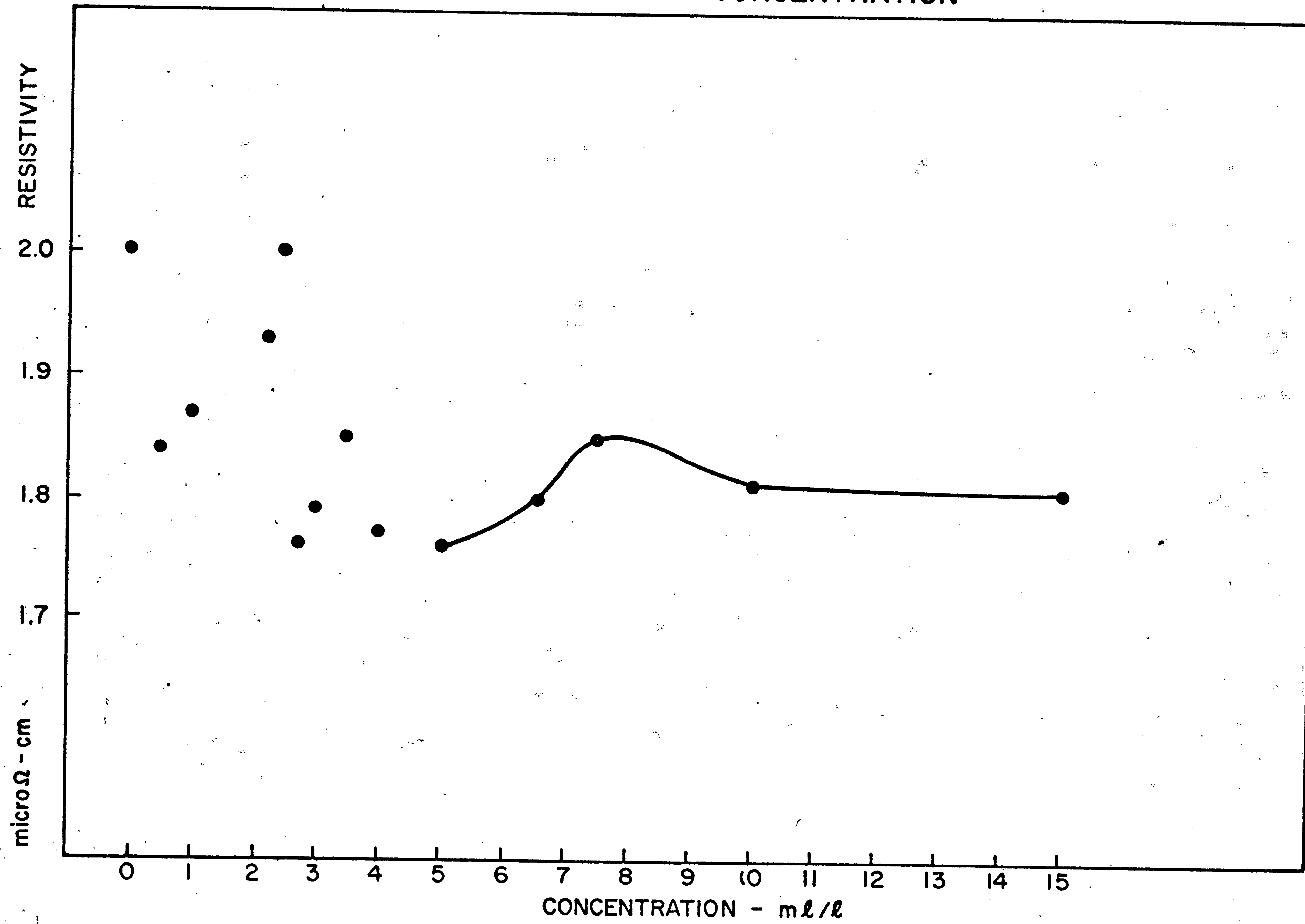


FIGURE 9.

below 4-5 ml/1, resistivity exhibited no correlation with concentration. At concentrations 5 ml/1 of additive and greater the resistivity is fairly constant.

The price of leveling in terms of observed properties is small provided a minimum concentration of 5 ml of Cubath Hy per liter of $Cu(BF_4)_2$ is utilized. Tensile strength for the additive bath deposit is equal or greater than the non-additive deposit. Ductility is only slightly decreased by the additive. An improvement in electrical properties is obtained in that the resistivity of the additive deposit was lower than the non-additive deposit resistivity.

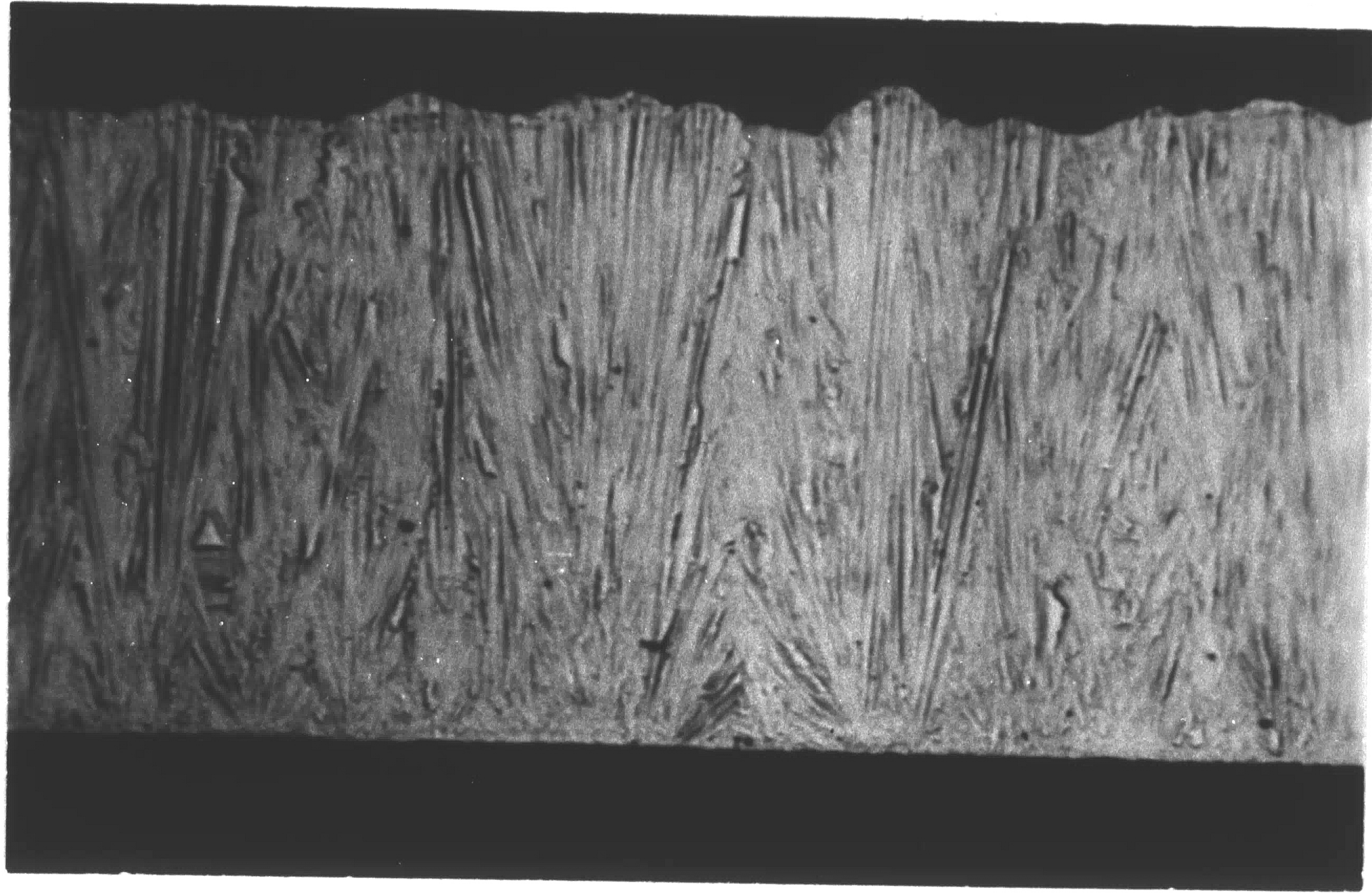
IV. THE RELATIONSHIP BETWEEN STRUCTURE & PROPERTIES

Variation of observed properties with additive concentration has been established. These property variations suggest a possible alteration in the structure of the electrodeposited copper.

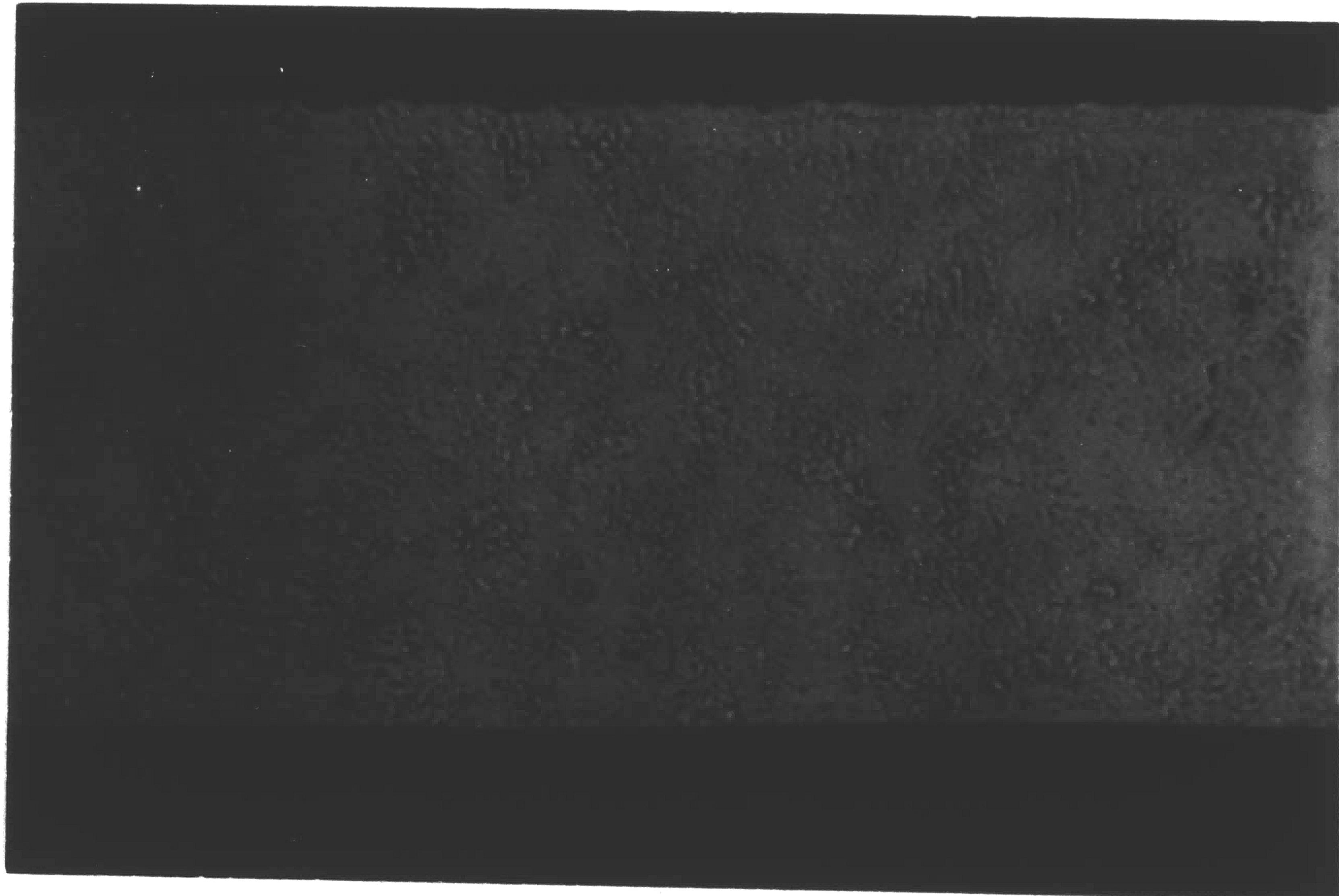
Micrographs were made of the structure of each at the selected additive concentrations. Two distinct structures were observed--a columnar structure and a fine grain structure. The columnar structure shown in Figure 10a is the structure produced by the non-additive bath and also the additive bath up to a concentration of 2.0 ml/l of Cubath Hy. This is the structure for cupric fluoborate deposits reported and illustrated in the literature.[3,4,7,8,15,16] The fine grain structure shown in Figure 10b is the structure produced by the plating baths containing 4 ml/l or more of Cubath Hy. Fine grain deposits from $Cu(BF_4)_2$ have been suggested in the literature,[7,9,14,26] with and without the use of organic additives. The structure shown in Figure 10b is the result of the chemical etching method employed. An obvious grain structure is not evident, but it is not columnar. Since the structure was too fine to be resolved with the methods employed it will be called a fine grain structure.

The concentration limits of 2.0 ml/l and 4.0 ml/l define the structure transition range. Some micrographs in this transition regime exhibit a composite fine grain and columnar structure.

The correlation between microstructure and observed properties is definite. With the addition of Cubath Hy to the bath, the properties of surface roughness, resistivity, tensile strength, ductility



A. COLUMNAR MICROSTRUCTURE



B. FINE MICROSTRUCTURE

FIGURE 10. PHOTOMICROGRAPHIC CROSS-SECTIONAL VIEWS OF DEPOSIT MICROSTRUCTURE

500X

C. COLUMNAR AND FINE MICROSTRUCTURE

FIGURE 10 CONTINUED

change from the initial values produced by the non-additive bath. The initial microstructure is columnar. At a certain additive concentration the structure is observed to change to fine. At concentrations of 5 ml/l and higher all the investigated properties are observed either to undergo only small changes or follow a definite trend. In addition the microstructure is fine grain. At 5 ml/l and above, average surface roughness drops below the maximum allowable value of 20 μ-in, resistivity stabilizes at approximately 1.8 $\mu\Omega$-cm, and average tensile strength recovers to a value above 42 kpsi and continues to rise. Ductility has recovered and stabilized at about 12% elongation. It is important to note that all this occurs after the structure chagge.

All observed properties of the deposit begin to alter with the addition of Cubath Hy to the plating bath. At concentrations of 5 ml/l and above the observed properties stabilize. However, in the initial additive concentration range of 1/2 to 4 ml/l little correlation between observed properties is evident. Resistivity and surface roughness vary widely. Elongation appears to go through a minimum; however, the scatter is large. Tensile strength dips and significant scatter exists. The microstructure changes from columnar to fine. Surface morphology underwent a complete change from a rough, layered texture to a very even, slightly grainy surface when viewed at 2500x in the scanning electron microscope (Figure 5).

To further investigate the structure change and its effects, scanning electron micrographs of the tensile specimen fracture sur-

faces were taken. Two lines of investigation were followed. The first method was to observe the edge of the samples. It was noted during the tensile tests that some samples failed slowly and in tear. Failure in this case was found to initiate and terminate at the edges. The second approach was inspection of the fracture surface structure.

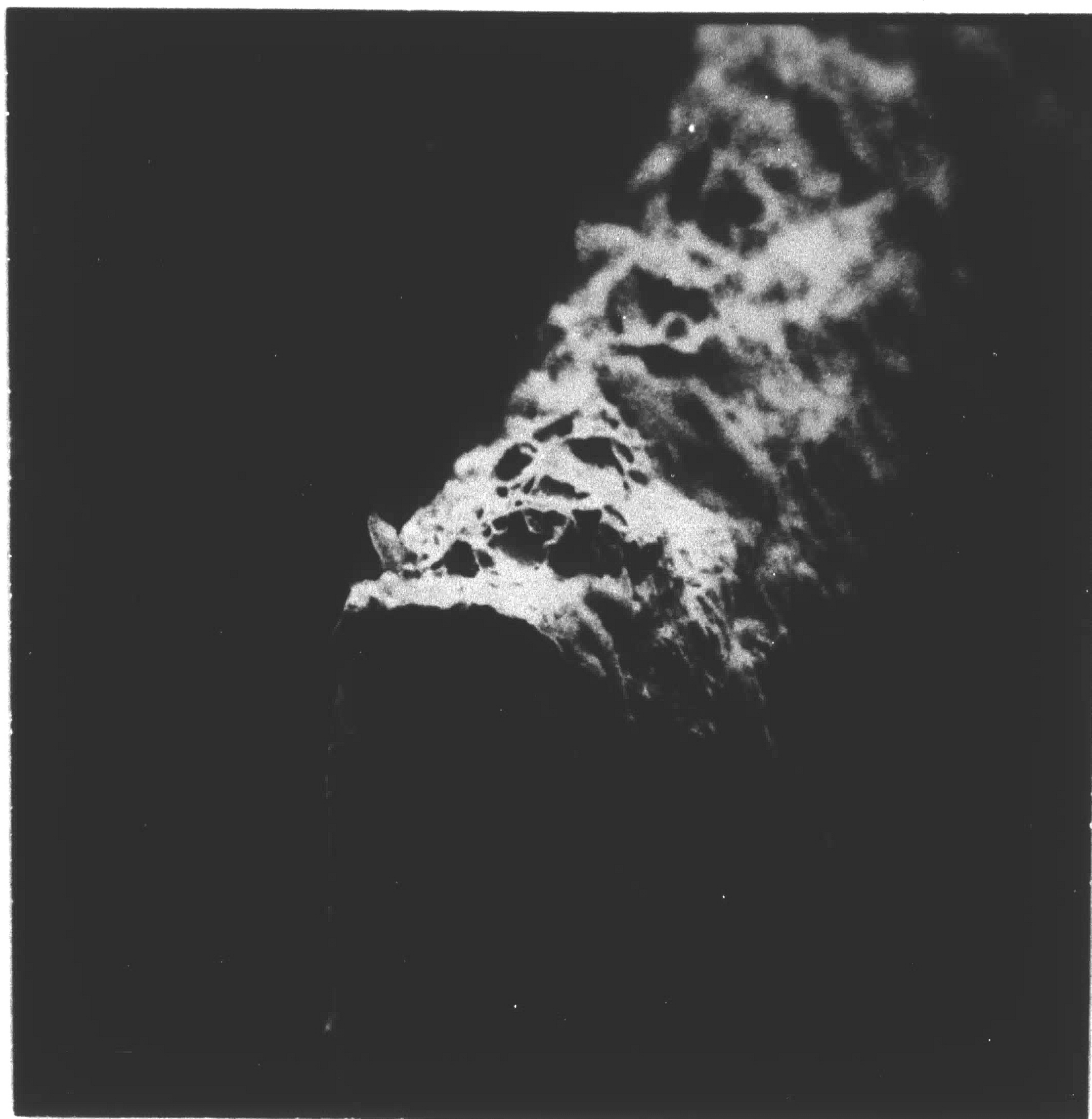
Figure 11 shows the topography at the sample edges. The blunt fracture surface of Figure 11a is typical of the non-additive deposit. If Cubath Hy in low concentrations is added to the bath, the fracture edge becomes tapered as shown in Figure 11b. At higher additive concentrations a sharp peak is formed as in Figure 11c. The transition from blunt to peaked end on the tensile fracture surface follows the changes in microstructure that occur with increasing additive concentration.

A peak formed at the ends of the samples from baths containing 2.5 ml/l of Cubath Hy or more. This peak continues across the sample, making the failure point an almost straight line across the micrograph. This line corresponds to 100% reduction in area at failure, and is exhibited by all samples produced at or above 2.5 ml/l additive.

Examination of the fracture surface struetuure shows changes with respect to additive concentration. Some variation in fracture surface topography between samples taken from the same sample plate was observed. However, a structure may be considered typical for a given additive concentration.

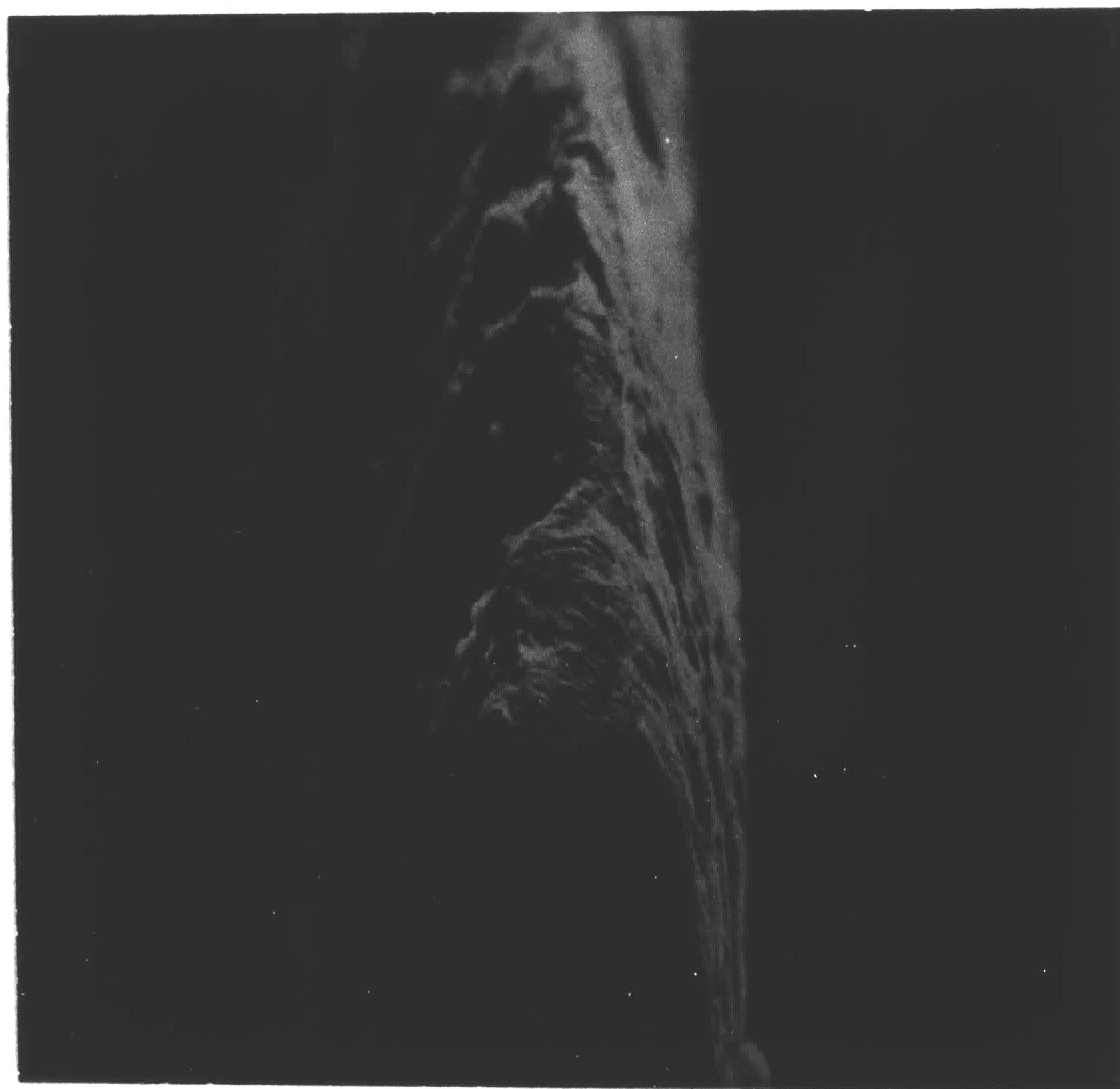
The fracture surface of the non-additive deposit is dimpled.*

*Terminology used follows Beachem and Meyn. Reference 28.



400X

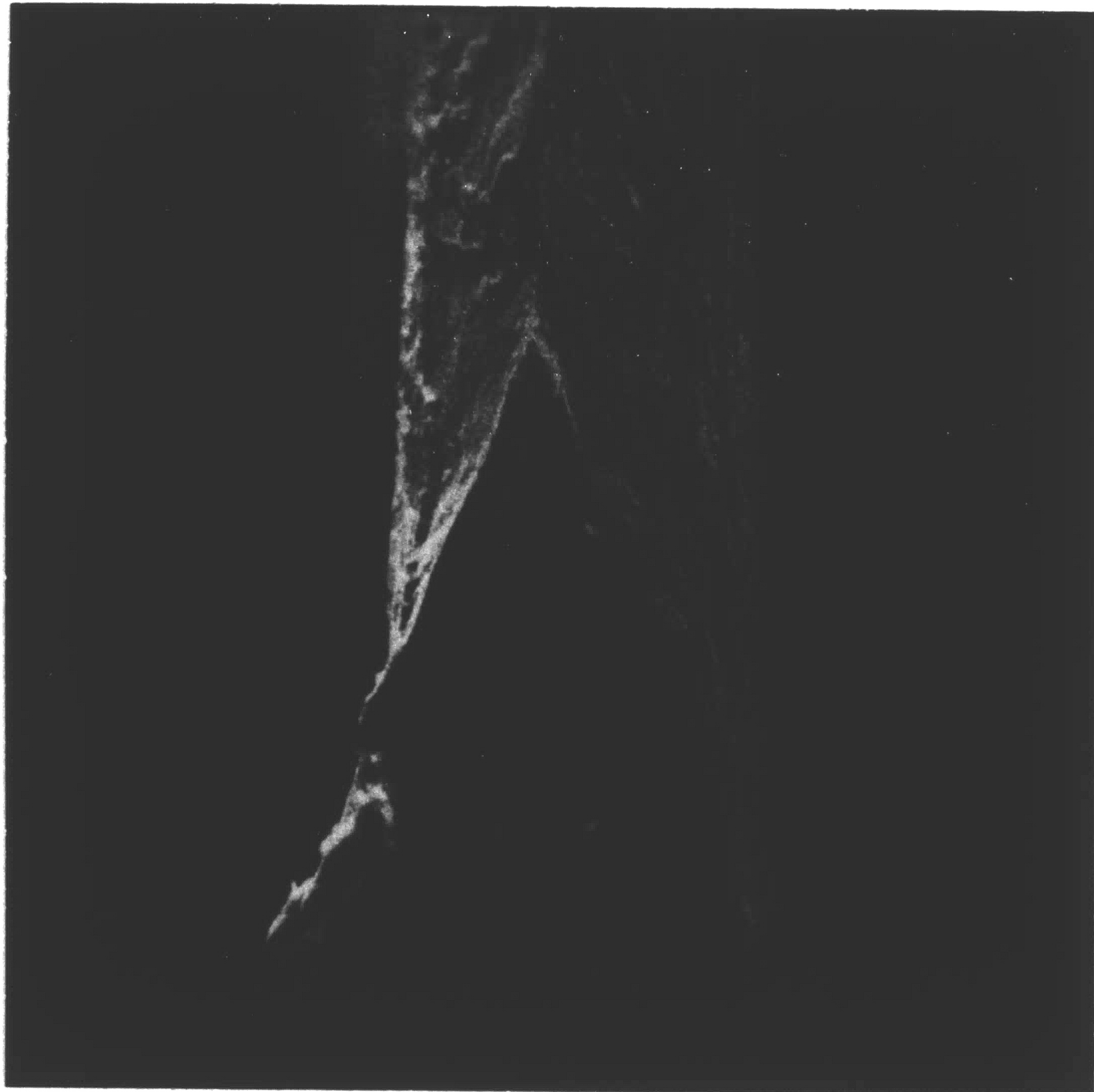
A. NO ADDITIVE - BLUNT



400X

B. LOW ADDITIVE CONCENTRATION - ROUNDED

FIGURE 11. SCANNING ELECTRON MICROGRAPHS OF TENSILE SAMPLE FRACTURE EDGE TOPOGRAPHY



400X

C. HIGH ADDITIVE CONCENTRATION - SHARP PEAK

FIGURE 11 CONTINUED

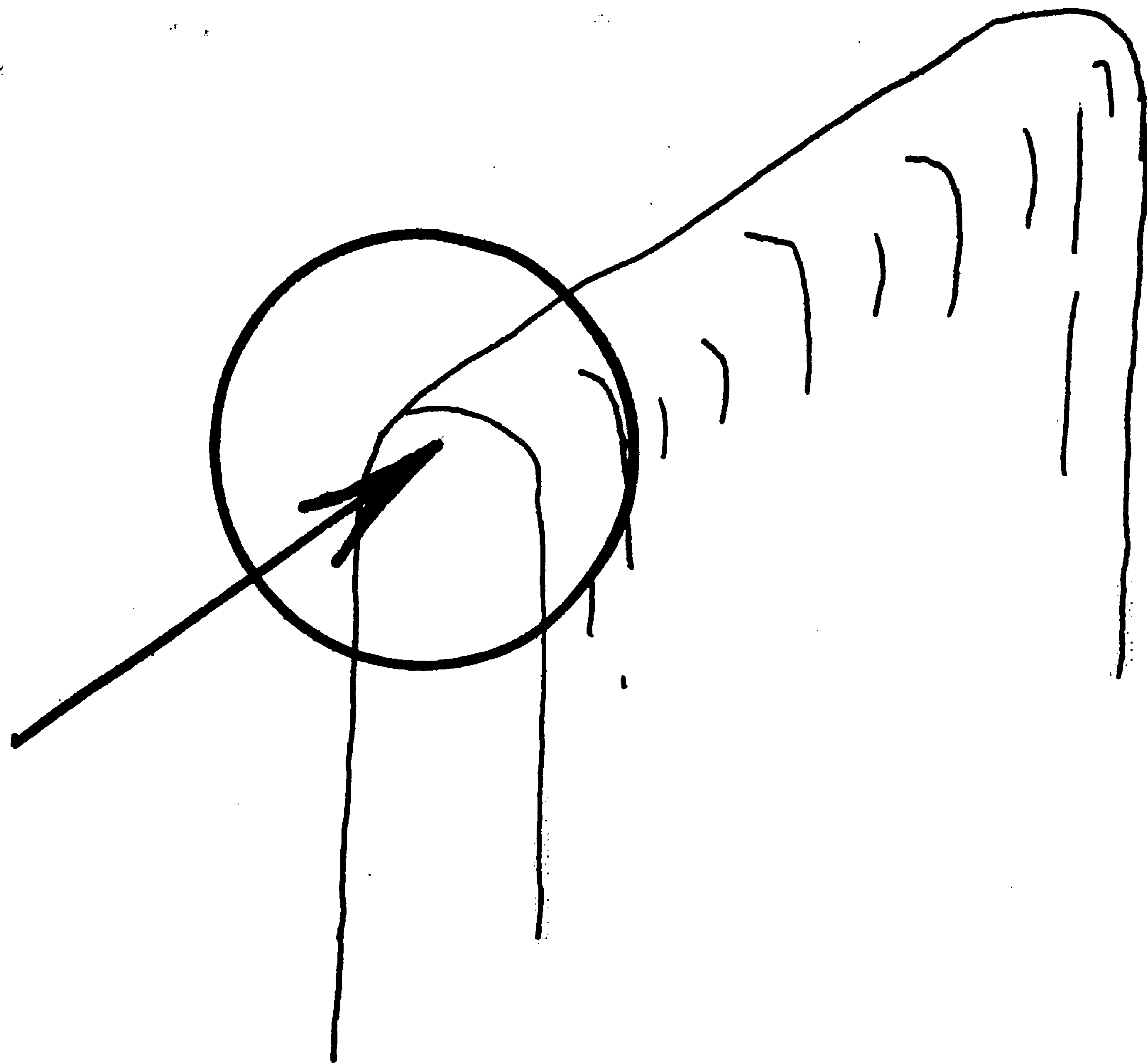


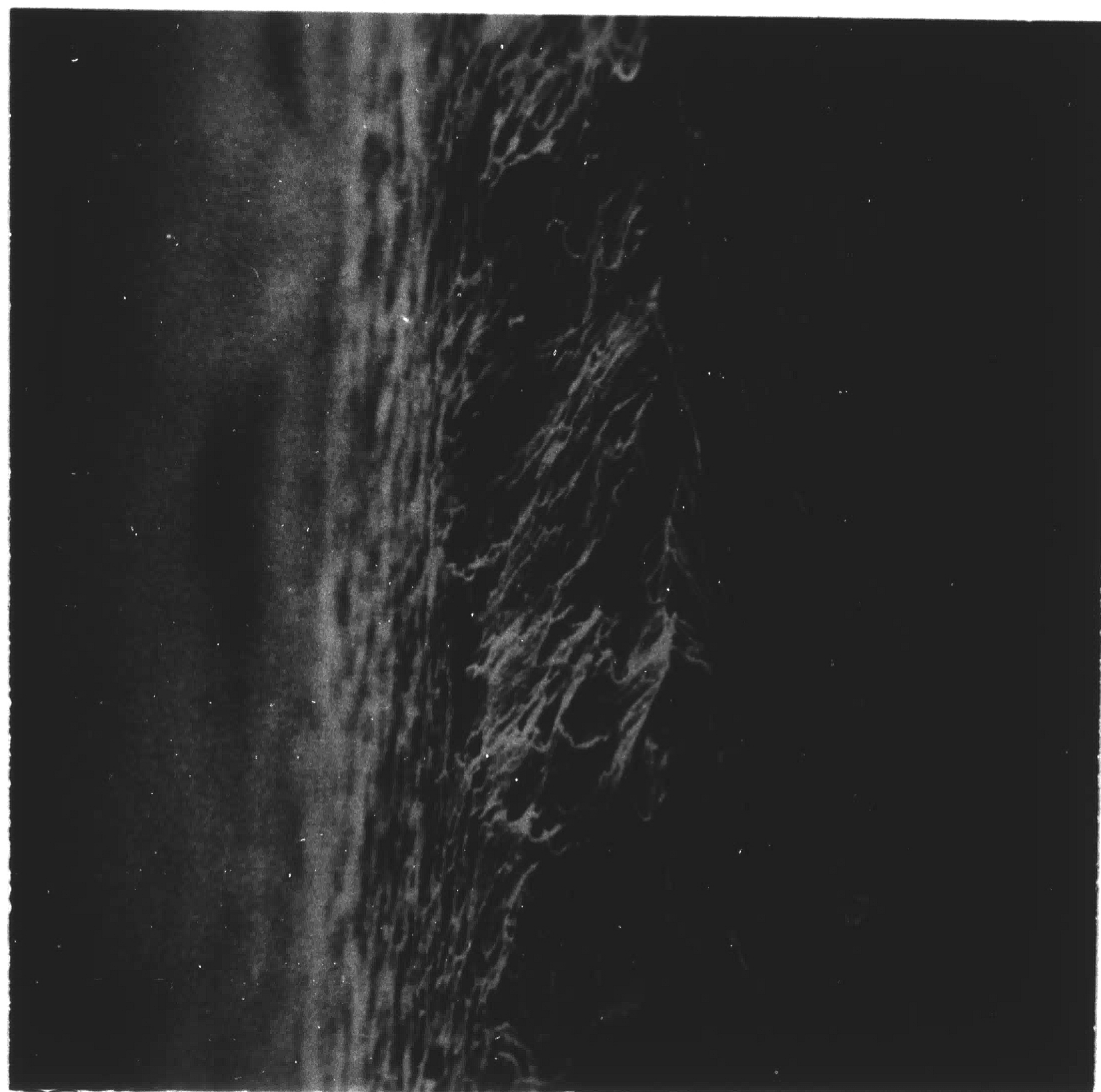
FIGURE 12. PERSPECTIVE OF SCANNING ELECTRON MICROGRAPHS OF TENSILE SAMPLE FRACTURE EDGE TOPOGRAPHY

The dimples are elongated as would be expected from the 15% elongation of the tensile specimen before failure. The failure mode is normal dimpled rupture (Figure 13a).

The fracture surface alters when the plating bath contained Cubath Hy. The changes which occur can be correlated to the changes in ductility and additive concentration. With the initial addition of Cubath Hy, the dimples become poorly defined and the apparent elongation much greater than the dimples in the non-additive deposit. As additive concentration is increased, the dimples become less evident, almost disappearing between 2.5 ml/l and 4 ml/l of additive. Dimples reappear at 4 ml/l of additive. These are highly elongated shear rupture dimples. This dimple structure is dominant at additive concentration of 5 ml/l or more. Tear dimples are seen at high additive concentrations, particularly at the point of failure (see Figure 13c). These dimples, whether shear ruptures or tear, are smaller than the normal rupture dimples of the non-additive bath samples.

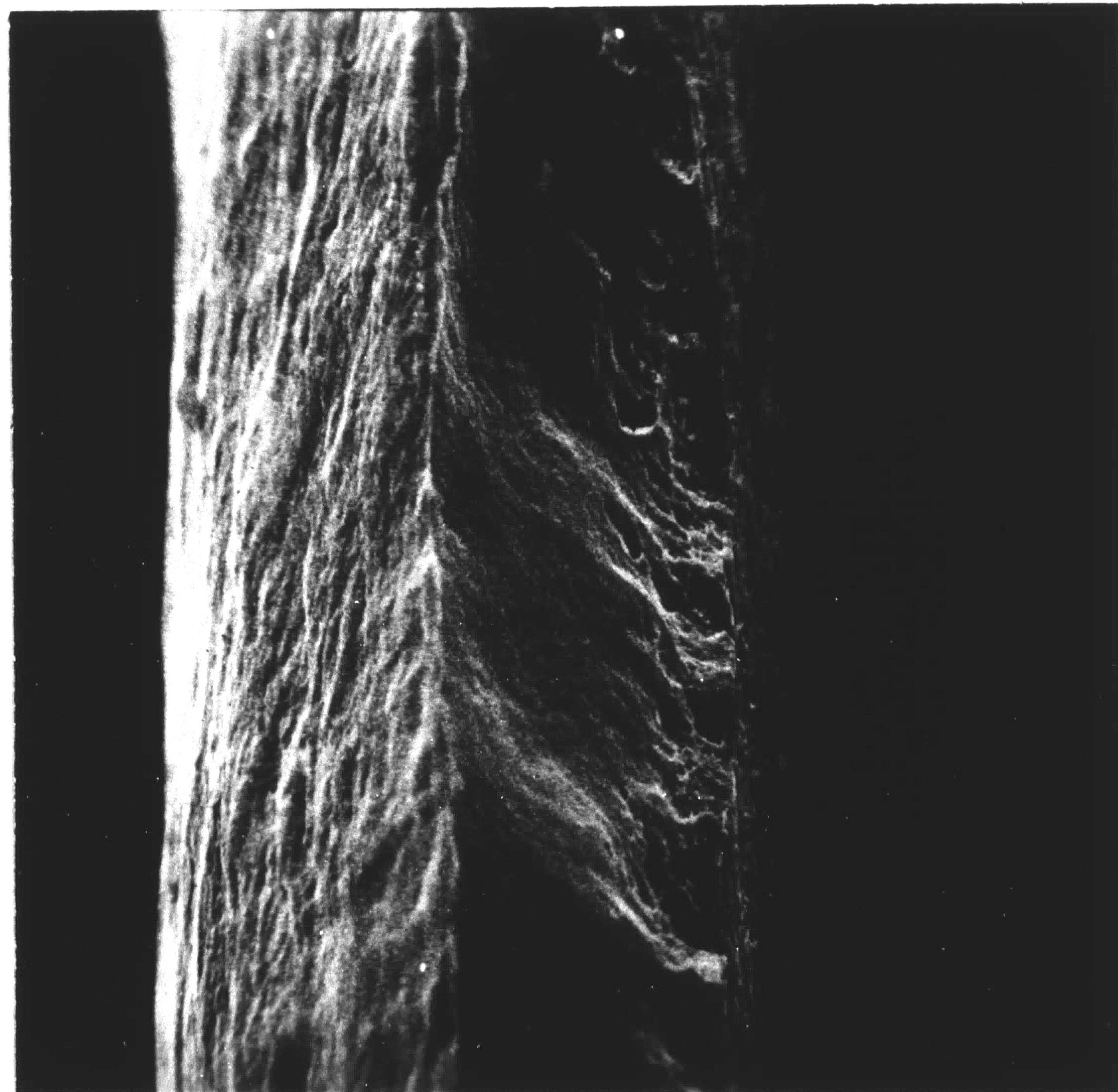
In the 1/2 - 4 ml/l concentration range the mechanisms of microvoid coalescence corresponding to extreme plastic strain[28] are evident. In order of increasing localized strain these phenomena are serpentine glide, ripple, and stretch (see Figure 13b).

A ridge appears on the substrate side of the deposit in many of the fracture samples. This ridge (Figure 13b) is below the failure point and exhibits a stepped or coarse granular structure. The fracture surface of this ridge is characteristic of a less ductile fracture than observed elsewhere on the samples. Above the ridge the surface



500X

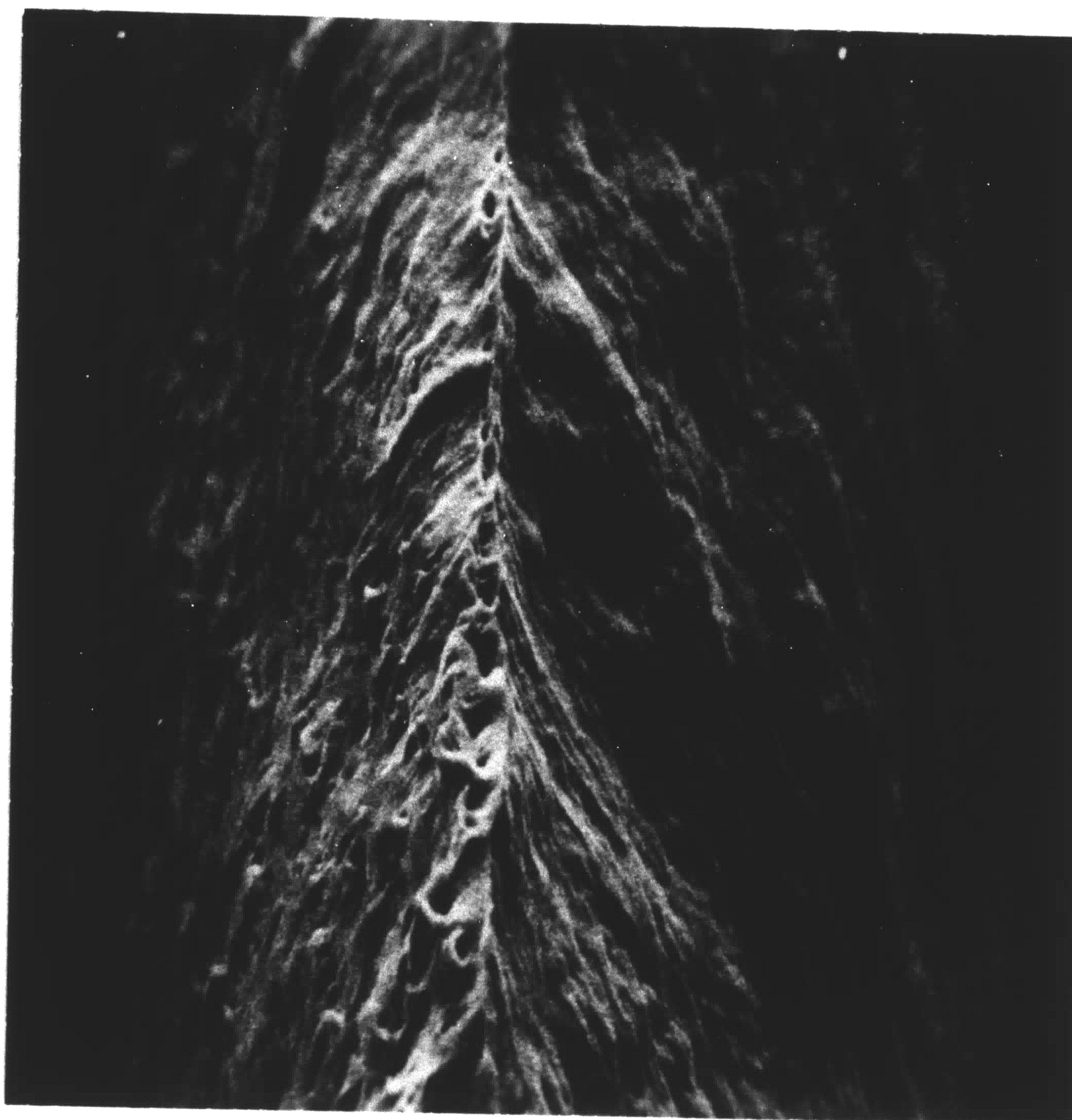
A. DIMPLED RUPTURE



600X

B. GLIDE AND STRETCH WITH RIDGE

FIGURE 13. SCANNING ELECTRON MICROGRAPHS OF FRACTURE SURFACE MORPHOLOGY



1000X

C. TEAR DIMPLES AT PEAK

FIGURE 13 CONTINUED

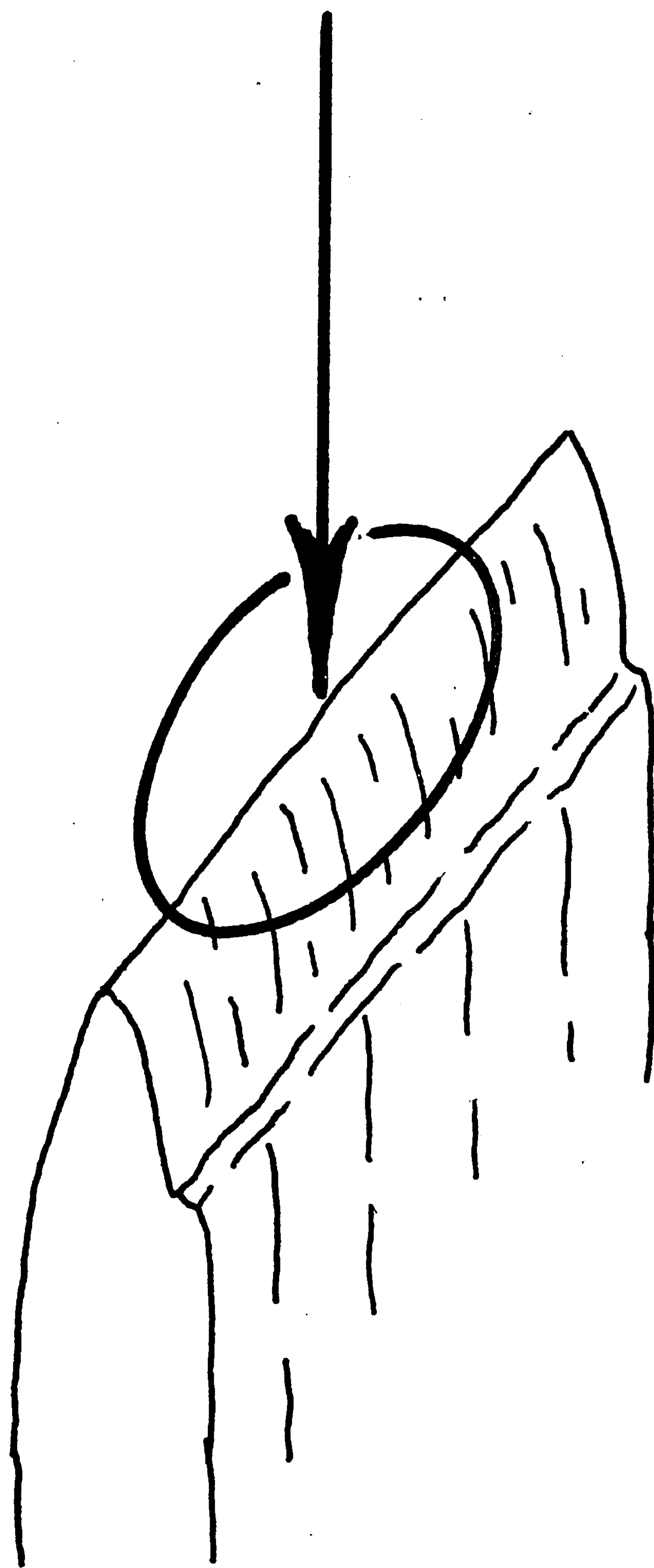


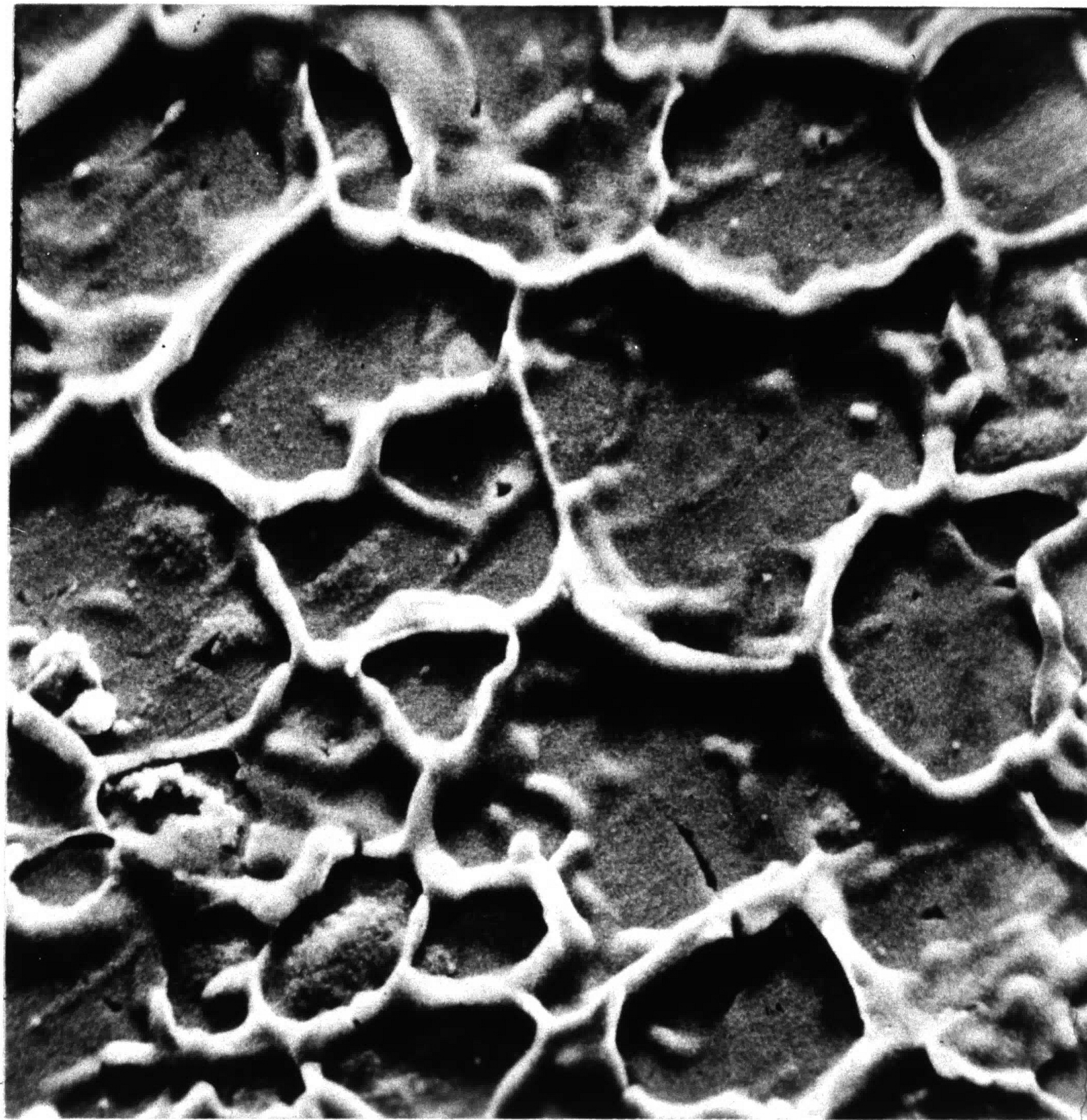
FIGURE 14. PERSPECTIVE OF SCANNING ELECTRON MICROGRAPHS OF FRACTURE SURFACE MORPHOLOGY

shows either ripples or stretch, varying between samples. The other side of the sample exhibits serpentine glide or ripple, but always a coarser structure than the area above the ridge. Since final failure has been observed to occur at 100% reduction in area, it is believed the metal above the ridge must have failed first. This would cause great localized stress in the adjacent material. This stress would be higher than that experienced by the nonsubstrate side material and greater localized plastic strain would occur above the ridge. This would account for the finer, smoother appearing surface.

In deposits from baths with more than 4 ml/l additive, the ridge, if present, is less obvious and often fragmented. The additive concentration range of 1/2 to 4 ml/l where the ridge is prevalent on the fracture surfaces of the deposits corresponds to the transition zone of the microstructure.

A clear correlation between fracture surface and Cubath Hy concentration was observed. However, the relation between fracture surface and ductility was not equally evident. For the non-additive bath samples and samples from baths containing up to 1 ml/l of additive, the ductility was high, averaging around 15%. With increased Cubath Hy concentration, up to 4 ml/l, the ductility of the deposit drops, reaching a minimum average ductility of 3%. This is the range where no dimple structure is in evidence, and the serpentine glide, ripple, and stretch patterns are observed. A dimpled structure appears again in deposits from baths containing 5 ml/l or more of Cubath Hy. Here the ductility has recovered and stabilized about a value of 12%.

To investigate possible gross mechanisms operating on or within the sample as the microstructure changed, SEM micrographs were made of the substrate side of the deposits (Figure 15). These were examined for voids and other evidence of variables as a function of additive concentration or microstructure. The deposit was found to replicate the substrate surface in every case with no significant variations in morphology.



2500X

FIGURE 15. SCANNING ELECTRON MICROGRAPH TYPICAL OF SUBSTRATE SIDE OF DEPOSIT

V. WHY LEVELING OCCURS

It has been established that leveling can be achieved and correlations exist between leveling and the mechanical and physical properties. These observations and correlations suggest mechanisms by which leveling may occur and why properties are affected.

LEVELING

Microleveling and macroleveling have been shown to be properties of deposits from $Cu(BF_4)_2$ electroplating baths when Cubath Hy is used as an addition agent. This has been shown by surface roughness measurements, leveling of a standard rough surface, and SEM micrographs of the deposit surface. Leveling appears to follow the theory of preferential additive codeposition and inhibited deposition.[17,19-23] This calls for the additive to be codeposited or absorbed into the deposit in areas of high current density and restrict further plating in these areas. High current density areas correspond to the peaks on the microleveling samples. The filling of the lands between the peaks as seen in Figure 2 is evidence of inhibited deposition, as the decreasing surface roughness is demonstrated in Figure 4 and 5. Plating efficiency (Figure 6) was seen to fall with increasing additive concentration. This follows the findings of Milora[8] that Cubath Hy decreases the diffusion coefficient of $Cu(BF_4)_2$ by about 10% at a concentration of 3.0 ml/l.

Leveling and microstructure are functions of additive concentration in that a structure change occurs beyond a certain concentration. Before the critical concentration (between 2.0 and 2.5 ml/l of Cubath

Hy) is reached, the microstructure is the typical columnar grain structure. These columnar grains extend from the substrate to the surface of the deposit. At the critical concentration and beyond it is believed that the codeposited additive interferes with the growth of the columnar grains. New grains are nucleated around the high current density areas where the additive is preferentially deposited, and a fine grain structure is formed. Supporting evidence for this is seen in dual columnar, and fine grain structures visible in Figure 2a and Figure 10c. Only the fine structure is seen at additive concentrations of 4 ml/l and up (Figure 10b).

RESISTIVITY

Resistivity varies as a function of additive concentration. Beyond the transition range of Cubath Hy concentration, the resistivity is fairly stable. In the transition range it fluctuates widely. It is believed that the resistivity varies with changes in the degree of perfection of the deposit. A changing, dual microstructure would cause variations in electron scatter sites from variable grain size and dislocation densities. This changing structure is seen in the micrographs of Figure 10.

DUCTILITY

The ductility of the deposit is affected by addition of Cubath Hy to the bath. Ductility is seen to vary as a function of additive concentration and, therefore, structure. The effects of the structure transition are quite evident. As Cubath Hy is added to the bath, the ductility of the deposit begins to change. In the transi-

tion range the scatter is high and the variation in the data with changing concentration is large. Beyond the structure transition range the ductility is fairly stable. This effect may be attributed to the variation in grain size and structure. With no additive in the bath the deposit has a homogeneous columnar structure and good ductility. As the structure changes ductility drops. Beyond the additive concentration range of the transition zone, the grain structure is once again homogeneous and ductility has recovered. The decreased ductility in the transition range is believed due to the inability of the dual structure to slip and deform plastically over relatively large areas. The mechanism of the deposit's changing ability to deform without rupture is seen in the fracture surfaces. Dimpled rupture occurs in the non-additive deposit. With the addition of Cubath Hy fracture mode alters. Highly localized deformation is observed in the forms of extreme microvoid coalescence[28]—serpentine glide, ripple, and stretch. As Cubath Hy concentration is increased to the high end of the transition range and above, the localized deformation decreases; dimpled rupture as shear and tear reappear, and ductility is observed to recover.

STRENGTH

Tensile strength is observed to vary as a function of additive concentration. From its initial, non-additive value, tensile strength drops as Cubath Hy is added to the bath, then recovers and goes higher than the initial value as increasing amounts of additive are added to the bath. Tensile strength is highly variable and shows little cor-

relation to other properties in the additive concentration range where structure varies. At additive concentrations above the transition range tensile strength increases slowly but smoothly with concentration. From the studies of failure mode the samples which failed from dimpled rupture exhibited the greatest strength. Those samples showing high localized deformation were observed to have variable, but generally lower strength. The fine microstructure consistently produced a tensile strength equal to, or greater than the non-additive columnar structure.

It has been shown that the addition of Cubath Hy to the plating has an effect on the deposit at all the concentrations studied. Resistivity is the most sensitive to small amounts of the additive. All properties varied significantly in the additive concentration range that corresponded to change in the microstructure. All observed properties correlate with the change in microstructure. Surface morphology and fracture mode are also seen to follow the change in microstructure, although perhaps not as closely as the physical and mechanical properties.

A leveling deposit does result from the addition of Cubath Hy to a $Cu(BF_4)_2$ electrolyte. As a necessary part of leveling a change in microstructure occurred. The properties of the deposit vary as functions of the microstructure present as related to additive concentration. The concentration range of transition is the same for all properties except microleveling for which the different plating conditions required may explain the observed discrepancy.

For engineering use 10 ml/1 of Cubath Hy in $Cu(BF_4)_2$ produces a deposit at 150 asf with a good balance of properties. This concentration is beyond the unstable transition zone and allows a margin of additive depletion within a usable concentration range. It produces a deposit which levels, and whose physical and mechanical properties meet the requirements for flexible printed circuits.

VI. CONCLUSIONS

1. A number of physical and mechanical properties of the deposit from a cupric fluoborate electroplating bath were found to correlate with addition agent concentration.
2. Microleveling resulted through the use of Cubath Hy, an organic addition agent.
3. Average surface roughness was less than 20 μ-in. for all deposits from baths containing 4 ml/l or more of Cubath Hy.
4. A significant change in surface morphology occurred at addition agent concentrations of 2.5 ml/l and greater.
5. A change in microstructure from columnar to fine was observed. The transition occurred within the addition agent concentration range of 1/2 to 4 ml/l.
6. Ductility decreased with concentration of Cubath Hy of less than 3.5 ml/l, recovered with increasing concentration, and remained at about 12% for addition aagent concentrations of 5 ml/l and greater.
7. Resistivity was approximately 1.8 $\mu\Omega$-cm at addition agent concentrations of 5 ml/l and greater.
8. Tensile strength of the deposit decreased with concentrations of Cubath Hy of 1 ml/l or less, recovered with increasing concentration, and equaled the non-

additive deposit at 5 ml/l. Tensile strength was found to further increase with addition agent concentrations greater than 5 ml/l.

9. Fracture surface morphology under tensile loading underwent significant changes as a function of addition agent concentration.

10. Relative plating efficiency decreased with increasing addition agent concentration.

APPENDIX I - EXPERIMENTAL PROCEDURE

I. Hull Cell

A Hull cell test was used to initially determine the useful additive concentration range and current density values.

To prepare the Hull cell for use the cell was treated in ~35% HNO_3 for one hour. Before every plating test the cell and anode were thoroughly rinsed with hot water, deionized water, treated for a minimum of 3 minutes in ~25% HBF_4, and rinsed in deionized water.

The sample was plated on brass cathode panels using the following procedure:

1. Peel protective plastic coating from brass panel.
2. Immerse in chemical polish until surface appears clean.
3. Rinse in deionized water.
4. Immerse in ~15% HCl for 3 minutes.
5. Rinse in deionized water.
6. Check wetting by immersing panel in water, removing, and holding in a vertical position. If water on the surface does not break within 30 seconds, wetting is complete. If panel does not wet, repeat from step 4.
7. Prepare bath by dilution 200 ml of stock $Cu(BF_4)_2$ with 100 ml deionized water in a graduated cylinder.
8. Add Cubath Hy to bath as required.
9. Pour 267 ml of bath into Hull cell.
10. Position anode and cathode panel in cell, retaining with

10. Position anode and cathode panel in cell, retaining with plastic spring clip. Care was taken that the clips were not in contact with the bath.

11. Plate for 15 minutes at 5 amperes.

12. Rinse cathode plate in deionized water.

13. Dry with compressed air.

14. Determine current density.

The panels from the Hull cell tests indicated good results could be obtained using the chosen additive, Cubath Hy, and 150 asf plating current density. An additive concentration range of 1/2 to 15 ml/l was found to provide acceptable results and was employed for further studies.

II. Plating Cell Cleaning

The 1 1/2 liter cell and the 7 1/2 liter cell were initially prepared for use in the following manner.

1. Flush in hot, running water for 30 minutes.
2. Rinse with ~10% HNO_3.
3. Treat with ~25% HBF_4 for 48 hours.
4. Rinse with deionized water.

Before every plating experiment, the following cleaning steps were executed:

1. Flush with hot water.
2. Rinse thoroughly in deionized water.
3. Treat with ~25% HBF_4 for 5 minutes.
4. Rinse with deionized water.

The plating cells were treated for 5 minutes with ~35% HNO_3 after every third or fourth plating experiment.

Anodes were prepared by the following steps.

A. Initial degreasing:

1. Immerse in trichloroethane for 3 minutes minimum.
2. Immerse in acetone for minimum of 1 minute.
3. Rinse thoroughly with deionized water.

B. Before every plating experiment:

1. Rinse with deionized water.
2. Immerse in chemical polish until a shiny surface appears.

3. Rinse in deionized water.

4. Place in HBF_4 for at least 3 minutes.

5. Rinse with deionized water.

The polypropylene anode bags used with the anodes in the large plating cell were initially flushed for 30 minutes in hot water, rinsed in deionized water, treated in ~25% HBF_4 for 24 hours, and rinsed with deionized water. Between each plating experiment the following procedure was applied to the anode bag.

1. Rinse thoroughly in hot, running water.
2. Rinse in deionized water.
3. Treat in hot HNO_3 (~35%) until all visible trace of sludge and oxide disappears.
4. Rinse in deionized water.
5. Treat in ~25% HBF_4 for 3 minutes.
6. Rinse in deionized water.
7. Place cleaned anode in bag.

III. Plating Bath Preparation

The as-received cupric fluoborate plating both was first pumped through a carbon stone filter. Two parts $Cu(BF_4)_2$ (~180 g/l of copper) were diluted with one part water which had been deionized to a resistivity of greater than 10^{18} megaohms. The plating solution was prepared in 5 gallon lots.

Microleveling samples required 1500 ml of plating solution. These samples were prepared using Cubath Hy in concentrations of 0.0, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 6.6, 7.5, 10.0, and 15.0 ml per liter of $Cu(BF_4)_2$. Large plating samples needed 7 liters of plating solution. Samples were produced with 0.05, 1.0, 2.0, 2.5, 2.75, 3.0, 3.5, 4.0, 5.0, 6.6, 7.5, 10.0 and 15.0 ml of Cubath Hy per liter of $Cu(BF_4)_2$. The additive was added to the plating solution within 15 minutes of use.

IV. Sample Preparation

A. Microleveling Samples

The metal record stamper were cut to one square inch sample size and the following sequence of operations executed. All cleaning step times are minimum.

1. Degrease by immersing samples in:
   a) Trichloroethane for 2 minutes.
   b) Acetone for 1 minute
   c) Rinse in deionized water.
2. Solder 6 in. copper wire to back of sample.
3. Degrease as in step 1.
4. Dip in chemical polish for 1 minute.
5. Immerse in trichloroethane and acetone for 1 minute each.
6. Rinse in deionized water for 1 minute.
7. Activate surface for 3 minutes in 15-20% HCl.
8. Rinse in deionized water.
9. Dry with compressed air.
10. Mask back of sample with plater's tape.
11. Insert sample into plating fixture.
12. Immerse in 25% HBF_4 for 1 minute.
13. Rinse in deionized water.
14. Fill plating cell with prepared plating solution.
15. Position anode with 1 1/2 inches below the liquid surface.

16. Position sample holder with sample 1 in. below bath level.

17. Position stirring rod near one side of plating cell and set motor speed control to 65.

18. Plate sample for 38 minutes at 1.05 amps.

19. Remove sample from fixture and rinse in deionized water.

20. Plate in nickel bath for 30 minutes as protection during subsequent metallurgical preparation.

21. Rinse in deionized water.

22. Dry with compressed air.

B. Large Scale Samples

Cathode plates were cut from a 3/32 in. thick 304 stainless steel sheet to a 6 1/2 x 9 in. size. The plates were cleaned and prepared as follows. Times specified are minimum.

1. Wash with soap and water.
2. Place in boiling trichloroethane for 5 minutes.
3. Dip in acetone for 1 minute.
4. Rinse in deionized water.
5. Passivate in hot HNO_3 (~35%) for 45 minutes.
6. Rinse with deionized water.
7. Dry with compressed air.

A 6 x 6 1/8 in. rectangular was masked off with plater's tape. About 3/16 in. was masked off the bottom and sides of the cathode plate, and about 2 in. above the sample. The back was masked the same height as the front. After taping the plate was:

1. Immersed in ~25% HBF_4 for at least 3 minutes, and;
2. Rinsed in deionized water.

The equipment was prepared for use in the following manner:

1. Pour approximately 6.5 liters of prepared plating bath into the plating cell.
2. Position anode and cathode in bath and fasten with plastic spring clamps. Bath should be 3/4 in. above the sample area on the cathode plate and about 6 in. of anode should be immersed.
3. Place the temperature control sensor in a corner of the plating cell near the cathode. Turn on the control unit.
4. Set the temperature control sensor between 25 and 26°C and adjust to maintain the bath temperature within ±1/2°C of the set point.
5. Clip the thermocouple for the temperature monitoring recorder to corner of the plating cell on the anode side. Thermocouple tip

should be at least 1 in. below the bath surface. Turn chart recorder on.

6. Turn on nitrogen and adjust flow to 15 scfm.
7. Start stirring motor and adjust speed and position for an even flow pattern across the cathode plate.
8. Turn on refrigeration unit and set to 15-18°C.

The samples were plated for 45 minutes at 38 amps. The sample was rinsed in a cascade rinse tank with air agitation. The sample was dried with compressed air and the plater's tape removed.

Hand contact with the samples was avoided subsequent to cleaning through the use of rubber gloves.

V. Testing

A. Microleveling

The record master samples were marked perpendicular to the grooves with the aid of a stereo microscope at low magnification. The samples were sheared along this line and mounted in epoxy. Standard metallographic polishing procedures were used and the samples etched with a solution of equal parts NH_4OH, H_2O, and H_2O_2 (3% by volume). The samples were photographed at 200x and 500x. Ridge heights and plating thicknesses over the ridges and lands were measured with a steel rule.

B. Surface Roughness

Surface roughness was measured as center line average with a Taylor-Hobson Talysurf 4.* Measurements were made with the sample on the stainless steel substrate. A minimum of 10 readings were taken on each sample plate—5 vertically and 5 horizontally, each at a different position.

C. Resistivity

Samples were removed from the substrate by inserting a scalpel blade under the edges and lifting gently. Nodules caused by uneven current distribution at the edges of the samples were removed by trimming 1/8 - 1/4 in. off each side. Sample strips about 5 3/4 in. long by 0.5 $\pm$ 0.010 in. wide were cut lengthwise (top to bottom with respect to orientation in the plating cell)

*Engis Equipment Co., Morton Grove, Illinois

with a double bladed cutter per ASTM E 345-69 for a Type B sample. Six or seven samples were cut from each sample plate.

Resistivity was determined using a Leeds-Northrup Kelvin Bridge and a 4-point knife edge probe. The knife edge spacing was 10 cm. Resistivity was measured twice on each of two samples from each sample plate.

D. Mechanical Testing

Tensile and elongation data was obtained with an Instron Model TM tester. The samples were tested in two groups. The first group employed both 3 and 4 in. gage lengths. Bolster plates of electrodeposited copper were fastened to the grip area with Eastman 910 adhesive. Samples were held in air operated serrated grips with 40-50 psi line pressure. The second group used a 4 in. gage length and smooth face grips with 80 psi line pressure.

The test conditions were as follows:

Chart speed	10/in/min
Chart scale	200 lbs full
Cross head speed	0.2 in/min

No significant difference was observed between the two groups.

E. Microstructure

Microstructure samples were taken from the centers of the sample plates. Samples were mounted in epoxy with an 800 mesh ceramic filler for edge retension. Samples were polished by standard methods and etched with the NH_4OH-H_2O_2-H_2O solution previously speci-

fied. Samples were photographed with a Leitz metallograph on Polaroid film.

F. Electron Micrographs

Scanning electron micrographs were made of the sample plate surface, the substrate side of the sample, and the tensile fracture surface of each sample plate. A Cambridge scanning electron microscope (SEM), operated at 20 KV in the secondary emission mode with a 45° stage tilt, was used. Surface samples were taken from the center of each sample plate. Fracture surface samples were observed by mounting 1/4 in. specimens vertically in groups. The photographs were made using Polaroid film.

APPENDIX II - APPARATUS

I. Small Scale Plating

A. Plating Cell

A 6 x 4 1/2 x 5 in. cell fabricated of 1/4 in. polypropylene was used. The cell capacity was 1500 ml.

B. Plating Fixture

A plating fixture was made from a 5 x 2 in. strip of 1/4 in. polypropylene. A 2 x 1/2 in. strip was welded to one end of the piece. Above this bottom strip a 2 x 1/2 in. strip was welded to form a 1 x 2 in. rectangle which would hold the sample with a light friction fit.

C. Anode

The anode was a 1 x 6 x 1/4 in. piece of oxygen free high conductivity (OFHC) copper.

D. Associated Equipment

1. Power supply[a*].

2. Stirring motor[b] and plastic stirring rod with 4-vane propellor.

3. Ammeter[c].

*Superscripts refer to the key in part III - Plating Equipment.

II. Large Scale Plating

A. Plating Cell

An 11 x 5 1/2 x 10 1/4 in. tank was fabricated of 1/4 in. in. polypropylene. Internal separators and constraints were provided to position a flexible heat exchanger bundle along the inside periphery of the cell. Lower positioning rails were provided for the anode and cathode plates.

Anodes were cut from OFHC copper sheet to a 6 x 9 in. size.

B. Temperature Control System

The temperature control requirement was ± 1/2°C of the set point. A Thermo -O-Watch[d] electronic controller with a 20-50°C thermometer was chosen as the basic feedback control unit. The section of the thermometer immersed in the plating bath was covered with thin Teflon heat shrinkable tubing. The electronic controller was connected to a circulating pump[e] in a tank which functioned as a chilled water reservoir. The water was cooled with a constant flow portable cooling unit.[f] The chilled water was pumped through a Teflon bundle heat exchanger[g] coil contained within the plating cell. Mixing was via mechanical agitation[h] and nitrogen bubbled through a polypropylene sparger tube (#74 holes). Temperature was visually monitored using a chart recorder[h] and an iron-constantan thermocouple covered with heat shrinkable TFE tubing.

In operation the electronic controller was set to the control

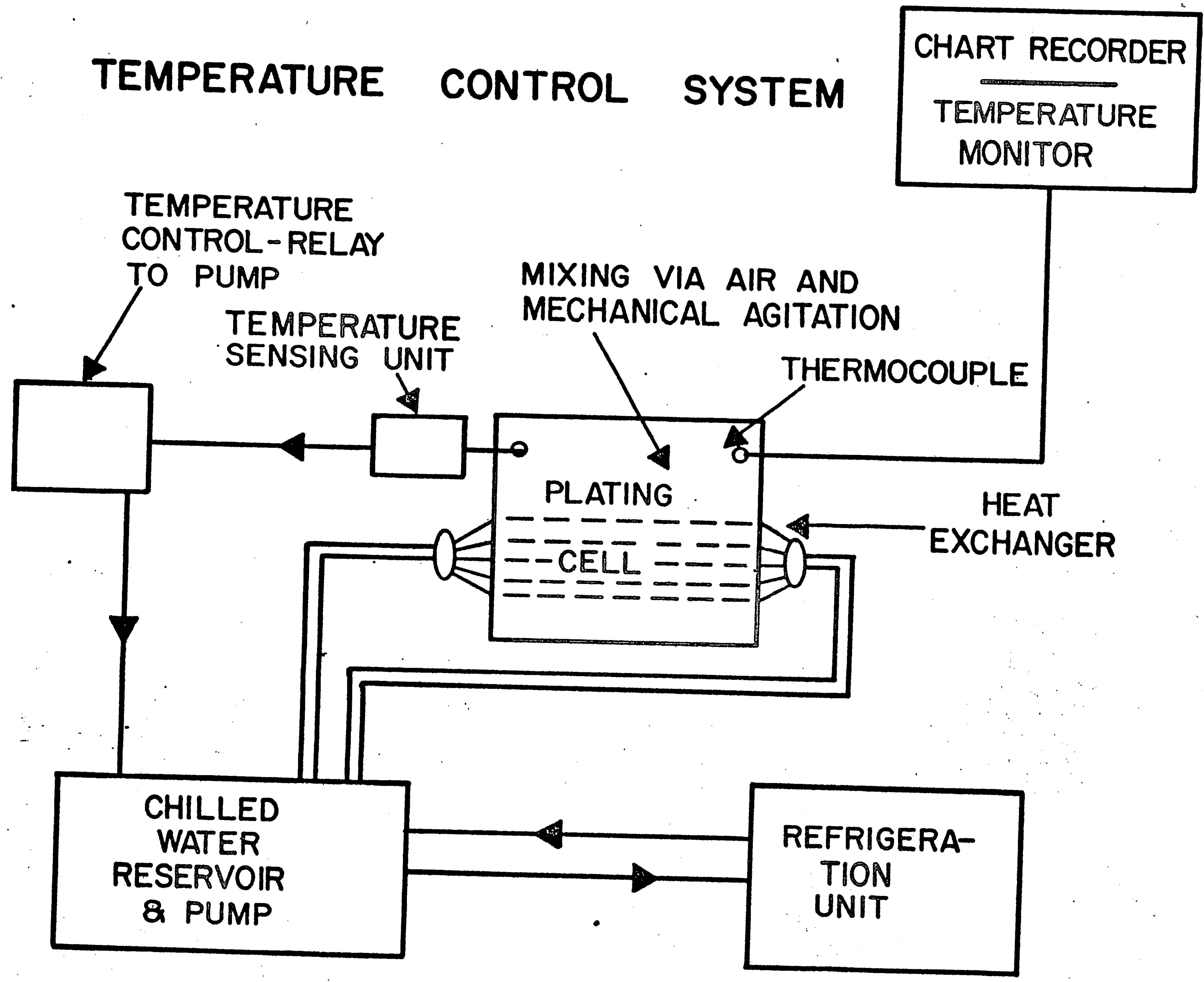


FIGURE 16.

temperature and the control band adjusted to less than $\pm$ 1/2°C.
temperat
When the bath temperature rose above the upper control unit, the sensing unit in the plating cell would activiate the relay to start the circulating pump. Chilled water was circulated through the heat exchanger in the plating cell, cooling the bath. When the bath temperature dropped below the lower temperature control point, the sensing unit activated the relay to cut off the pump. Visual monitoring with the cart recorder trace provided a verification of proper operation and relative control limits.

C. Associated Equipment

1. Power supply[i] - 0-60 amps.
2. Flow-control meter[j] - 0-50 scfh.

III. Plating Equipment

Key	Description	Manufacturer/Model
a.	Power supply	Kepco Current Regulator 0-2A
b.	Stirring motor	Talboy's Engineering Corp., Model 101
c.	Ammeter	Wessem Industries, Inc.
d.	Electronic temperature controller	I^2R, Model L-6
e.	Circulating pump & tank	Sethco Model ZDX-50 from Plating Products
f.	Portable cooling unit	Blue M Electric Co., Model PCC-24A-2
g.	Teflon bundle heat exchanger	E. I. du Pont
h.	Chart recorder	Varian, model A-4223A
i.	Power supply	Sorensen Nobatron, DCR40-60A
j.	Flow control meter	F. W. Dwyer, 0-50 scfh

IV. Test Equipment

A. Surface roughness - Talysurf 4, Taylor-Hobson by Engis Equipment Company

B. Kelvin bridge - Leeds & Northrup, Model 4287

C. Tensile tester - Instron Model TM with 200 lb. load cell

1. Serrated grips - Instron Type 1C

2. Smooth grips - Instron Type 3CA

V. Plating Supplies

1. Cupric fluoborate - 44-46% purified, Baker & Adamson
2. Fluoboric acid - 48-50%, Baker & Adamson
3. Cubath Hy - Stock No. 10,900 Sel-Rex Co.
4. Chemical polish - Chem-Polish 14, Shipley Co., Inc.
5. Acetone
6. Trichloroethane
7. Hydrochloric acid
8. Nitric acid
9. Plater's tape - No. 470-3VEA, 3M Company
10. Record stampers - Diskmakers, Inc.
11. OFHC copper

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