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## An investigation of the mechanism controlling the co-deposition of aluminas with copper during electrodeposition of copper

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## SUMMARY

Experimental work was undertaken to determine the mechanism controlling the co-deposition of aluminas with copper during electrodeposition of copper. The aluminas were present in the copper plating electrolytes as an insoluble disperse phase.

Three possible mechanisms for co-deposition of aluminas were studied. They were mechanical inclusion, electrophoretic deposition, and adsorption.

The results of experimental studies established that mechanical inclusion was not a significant factor in the mechanism controlling co-deposition of aluminas with copper.

Theoretical considerations of the compositions of the copper plating electrolytes indicated that co-deposition of aluminas by an electrophoretic mechanism was highly unlikely. The conclusions arrived at by theoretical considerations were substantiated by experimental measurements of the zeta potential of the aluminas.

The alumina content of the copper electro deposits was also studied as a function of the pH of the plating bath. The results of these tests in conjunction with sedimentation studies demonstrated the absence of an isoelectric point for the aluminas over the pH range studied.

The presence of thiourea in the electrolytic plating baths (a substance known to be adsorbed on a copper cathode during electrodeposition), profoundly affected the amount of alumina in the electrodeposit,

however, no adsorption of thiourea on aluminas in aqueous dispersions was detected.

AN INVESTIGATION OF THE MECHANISM CONTROLLING THE CO-DEPOSITION OF ALUMINAS WITH COPPER DURING ELECTRODEPOSITION OF COPPER

BY

JAMES E. HOFFMANN

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey  
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NEWARK, NEW JERSEY

JUNE, 1965

## PREFACE

This attempt to elucidate the mechanism whereby various aluminas co-deposit with copper during the electrodeposition of copper was prompted by previous studies made to investigate the possibility of producing dispersion hardened alloys by electrodeposition.<sup>1</sup>

If it would be possible to produce a dispersion hardened alloy of copper and alumina by electrodeposition, one might anticipate obtaining an alloy possessing both strength and high conductivity at elevated temperatures. Investigation of the mechanism of co-deposition of aluminas with copper was undertaken with the hope that knowledge of the mechanism would aid in the development of such an alloy.

It is to be understood throughout this paper that the word "co-deposit" does not necessarily imply an electrical phenomenon, but rather that the materials co-depositing, the various aluminas, are transported to and embedded in, the electrodeposited copper by some means.

I wish to gratefully acknowledge the guidance of Dr. C. L. Mantell throughout this investigation, and that of Runyon G. Ernst for his advice and assistance in analytical problems.

I am indebted to U. S. M. R. Co. Research Division for the use of research facilities without which this investigation would have been impossible.

<sup>1</sup> Final Report to International Copper Research Association  
Electrodeposition of Dispersion Hardened Alloys, Opie, W. R.  
Ernst, R. G., Hoffmann, J. E. May 1, 1964



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## CHAPTER I

# CONSIDERATION OF MECHANICAL INCLUSION AS THE CONTROLLING MECHANISM IN THE CO-DEPOSITION OF ALUMINAS DURING ELECTRO- DEPOSITION OF COPPER

### Introduction:

The term mechanical inclusion when used in reference to electro-deposition implies a mechanism of co-deposition which is wholly mechanical in nature; furthermore, the only forces acting on a particle are gravity and contact forces.

Such a particle is presumed to be electrically inert and incapable of any electrical interaction with electrodes in an electrolytic plating bath.

Commercial processes for electrolytic production of a metallic matrix containing a co-deposited phase by electrodeposition from a bath containing a disperse insoluble phase frequently state that co-deposition is caused by mechanical inclusion.<sup>2,3</sup> A. E. Grazen<sup>4</sup> makes the following statement:

"In essence, the process of the present invention involves simultaneous electrodeposition of a metal, and settling of electrically inert additive particles, under controlled conditions, to pro-

<sup>2</sup> U. S. Patent 2,878,171 Method of Manufacturing Abrasive surfaces by electro formation and the products obtained thereby. M. Ferrand 3/17/1959

<sup>3</sup> U. S. Patent 1,702,927 Bearing Material and Method of Making Same Fred K. Bezenberger 2/19/29

<sup>4</sup> U. S. Patent 3,061,525 Method for Electroforming and Coating Alfred E. Grazen 10/30/67

duce a composite structure in which the additive particles retain their discrete identity and are more or less homogeneously dispersed within the electroplated metal deposit. In describing particles as 'electrically inert' I mean that they do not become electrically charged during the plating operation."

### Theory

If settling, i.e. gravity, is the controlling mechanism for co-deposition of aluminas (specific reference is made to alumina in the Grazen Patent) then the following assumptions may be made:

- 1) The content of alumina in the electrodeposit should be enhanced by increasing the particle size.
- 2) The geometry of the system, that is the disposition of the cathode surfaces relative to the direction of the falling particles, should effect the alumina content of the electrodeposit.
- 3) In geometrically identical systems the chemical composition of the electrolyte employed should exercise no effect on the alumina content of the deposit; that is the alumina content should be the same in all cathode deposits irrespective of bath composition.

Experimental Procedure

In order to investigate the theory of mechanical inclusion as the controlling mechanism in co-deposition of aluminas during deposition of copper a modified bent cathode test was employed.

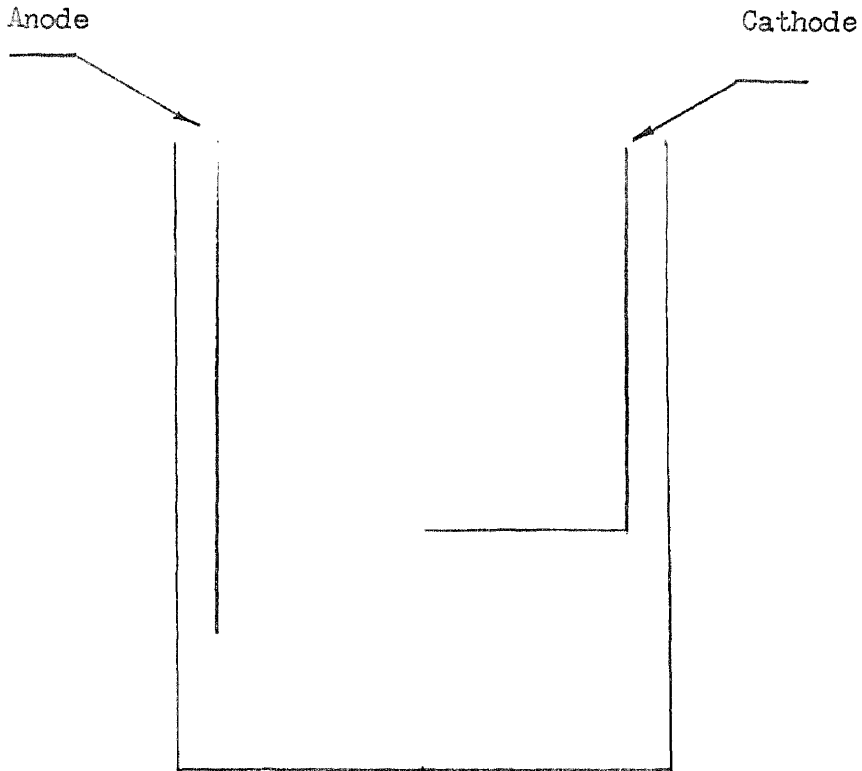


Fig. (1)

Bent Cathode Test Cell

The original bent cathode test<sup>5</sup> was used to evaluate the clarity of filter effluent in electroplating baths, by comparing the roughness of the deposit on the vertical surface with that on the horizontal surface.

<sup>5</sup> Sizelove, O. J. Monthly Rev. Am. Electroplaters Soc., Vol-16 p 15, 1929



It is apparent from figure (1) that two difficulties are inherent in this technique; 1, the current density on the horizontal portion of the cathode would be substantially greater than that on the vertical surface; 2, should the deposit obtained be rough, projections on the vertical face could act as horizontal planes and vitiate the relationship between the vertical and horizontal surfaces.

To obviate the problems inherent in the use of the bent cathode test, all vertical surfaces on the cathode were masked with electroplaters tape and deposition occurred only on the upper and lower horizontal faces of the cathode.

In order to test the validity of the third assumption made, namely that bath composition should have no substantial effect on the alumina content of the deposit, two different electrolytic baths were employed. The baths chosen possessed widely variant specific conductances, and substantially different pH operating ranges.

Description of Equipment and Apparatus. The tanks employed for the electroplating studies were rectangular pyrex battery jars 6.0" wide by 3-1/4" deep X 9-3/4" high.

The cathodes were fabricated from stainless steel 316 sheet of 0.030 inches thickness. The sheet was cut to dimensions of 7.5" X 1.75" and bent at right angles to form an L shaped cathode whose horizontal surfaces measured 1.75" X 3.0".

All edges and vertical surfaces were masked with Scotch Electroplaters Tape No. - 470.

The anodes were slices of electrolytic cathode copper 9" high by 2.25" wide by 0.5" thick.

In order to eliminate inordinately high current densities on the projecting edge of the cathode the anode was masked one inch above and below the projected line of intersection of the cathode with the anode. The exposed area of the anode was equal to that of the cathode, providing both with equal average current densities.

The agitator employed in the cell<sup>6</sup> was of pyrex glass and positioned so its center line was equi-distant from cathode and anode, and a plane passed horizontally through the center of the blade would be located equi-distant from the bottom of the cathode and the bottom of the deposition tank.

The assembled apparatus is depicted in Figure (2).

Description of Materials Employed in Experiment. The chemicals employed in preparation of the electrolytic baths are described below:

Copper Sulfate -  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  technical powder supplied by Fisher Scientific Co. Spectrographic Analysis of the salts, showed them to be substantially free of Sb, As, and Fe. Traces of Ni were present.

Sulfuric Acid -  $\text{H}_2\text{SO}_4$  reagent grade supplied by J. T. Baker Chemical Co., Specific Gravity - 1.84.

<sup>6</sup> The word cell encompasses the complete electroplating system.

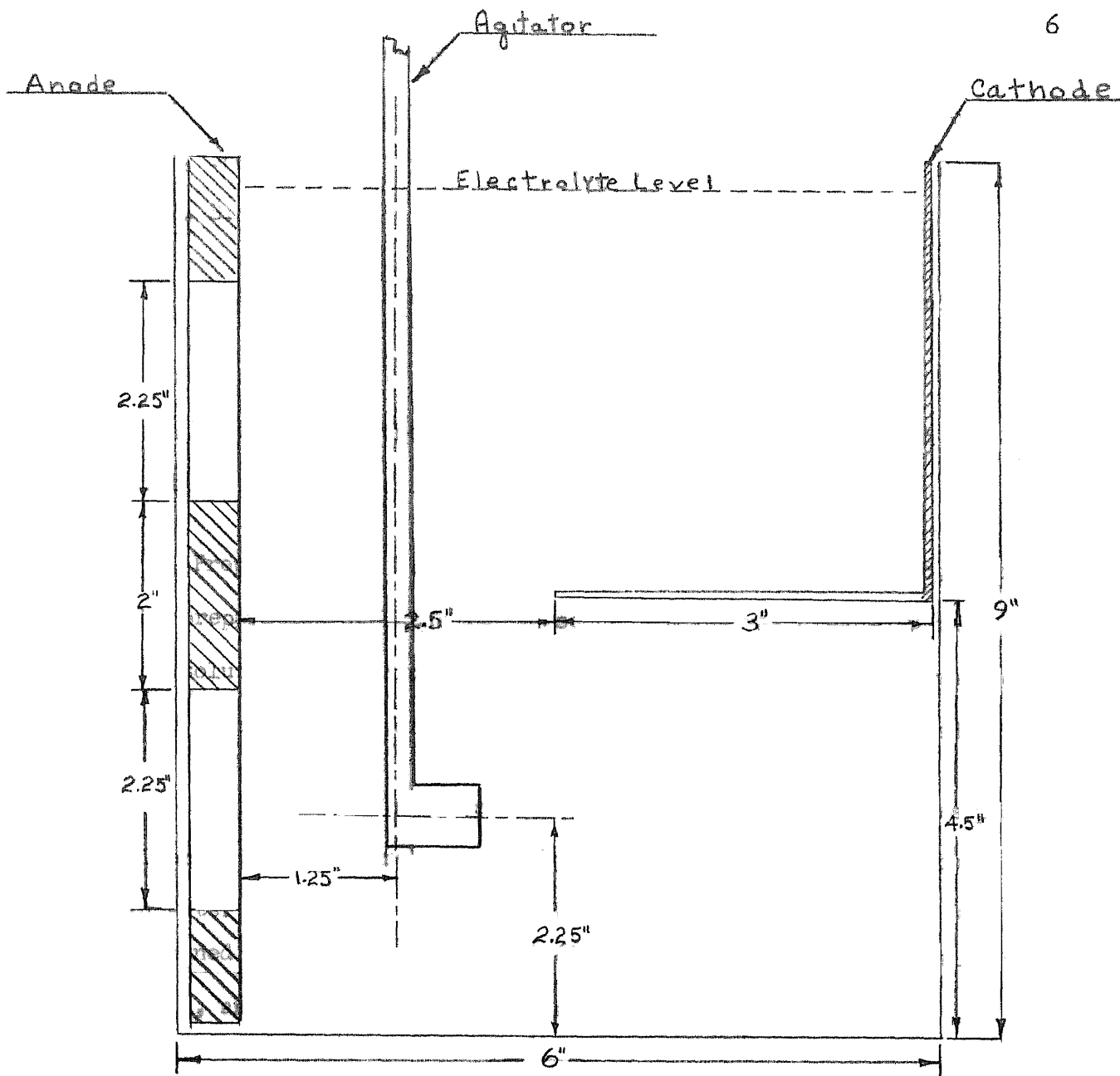


Fig. (2)

Deposition Cell for Studying the Effect of Mechanical  
Inclusion

Hatched areas on anode and cathode represent the area of the electrodes wrapped with electroplaters tape.

Ammonium Formate  $NH_4OOCCH$  reagent grade produced by reacting stoichiometric quantities of Fisher Certified reagent grade Formic Acid, Specific Gravity - 1.199 with 29% ammonium hydroxide, Dupont A. C. S. reagent.

Potassium Sulfate -  $K_2SO_4$  - Baker Analyzed Reagent, minimum assay  $K_2SO_4$  - 99.5%.

Water used in the preparation of plating baths was both double distilled and demineralized.

Preparation of Electrolytic Baths - All glassware employed in the preparation of baths and subsequent tests was cleaned with a hot solution of calcium hypochlorite, sodium hydroxide then washed with concentrated hydrochloric acid, tap water, then distilled water.

Copper Sulfate stock solutions of approximately 270 grams per liter  $CuSO_4 \cdot 5H_2O$  were prepared by dissolving the  $CuSO_4 \cdot 5H_2O$  powder in water and heating to 60° C. When a temperature of 60° C. was attained 70 grams of Darcomax G-60 powdered activated charcoal was added, and the solution was agitated for 1/2 hour at 60° C.

The solution was filtered by suction through Whatman 42 paper and stored in clean glass bottles until needed.

Preparation of the Copper Sulfate Sulfuric acid bath was accomplished by addition of sulfuric acid to the copper sulfate stock solution and dilution to the appropriate volume.

The preparation of the Copper Formate bath was accomplished by

dissolving the required amount of potassium sulfate in water, adding of the ammonium formate to the solution, then combining the above solution with the copper sulfate stock solution and adjusting to the appropriate volume.

The pH of the copper formate bath was adjusted to 4.0 by addition of ammonium hydroxide or formic acid; the quantity of either used was so small as to have no significant effect on bath composition.

The composition of the plating baths is set forth below:

#### Copper Sulfate, Sulfuric Acid Bath

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	-	188 grams per liter
$\text{H}_2\text{SO}_4$	-	74 grams per liter
pH	-	0.5

#### Copper Formate Bath

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	-	200 grams per liter
$\text{K}_2\text{SO}_4$	-	30 grams per liter
$\text{NH}_4\text{OOCH}$	-	30 grams per liter
pH	-	4.0

Aluminas employed as the disperse insoluble suspended phase in electrolytic studies were chosen so as to include materials of different particle size, bulk density, and method of preparation.

A description of the various aluminas is given below:

Properties of Aluminas Studied

Alon-C - almost chemically pure Alumina ( $\text{Al}_2\text{O}_3$ ) composed of extremely fine well defined particles. (Cabot Corp.)

The crystalline modification is gamma, a cubic structure.

The material was produced by vapor phase combustion of  $\text{Al}_2\text{Cl}_6$ .

Alon-C Product Data

Color - White

$\text{Al}_2\text{O}_3$ content - (moisture free)	-	95% minimum
Particle size range	-	0.01 - 0.04 microns
Surface Area Braunaur Emmett, Teller	-	50 - 100 square meters per gram
Sp Gr	-	3.3 - 3.6
Total non - $\text{Al}_2\text{O}_3$ oxides	-	0.2% maximum
Free moisture	-	2% maximum
Ignition loss - 1000°C	-	3% maximum
pH (10% aqueous dispersion)	-	4 - 5
Bulk density	-	3-5 pounds per cubic foot
Av particle diameter	-	0.03 microns

Linde - A - 5175 - Manufactured by Linde Co.

Chemical Formula -  $\text{Al}_2\text{O}_3$  (alpha modification)  
 Crystal System - Hexagonal  
 Hardness Mohs - 9  
 Particle Size - 0.3 microns  
 Surface Area (calculated) - 5.84 square meters per gram

The material was produced by calcination of high purity  $\text{Al}_2(\text{SO}_4)_3$  followed by comminution and classification.

The material is characterized by extremely uniform ultimate particle size.

Minimum $\text{Al}_2\text{O}_3$ content	-	99.9%	
Maximum impurities parts per million	-	Si - 60	Ga - 10
		Mg - 10	Cu - 10
		Pb - 70	Ag - 10
		Fe - 5	Na - 10
		Ca - 40	Ti - 10

Linde - B 5125 - Manufactured by Linde Co.

Chemical Formula -  $\text{Al}_2\text{O}_3$   
 Crystalline modification - gamma (cubic)  
 Hardness Mohs - 8  
 Particle size - 0.05 microns  
 Surface Area (calculated) - 14.2 square meters per gram

The material was produced by calcination of high purity  $\text{Al}_2(\text{SO}_4)_3$  followed by comminution and classification.

The material is characterized by extremely uniform ultimate particle size.

Minimum Al <sub>2</sub> O <sub>3</sub> content	-	99.9%	
Maximum unpurities parts per million	-	Si - 60	Cu - 10
		Mg - 10	Ag - 10
		Pb - 70	Na - 10
		Fe - 5	Cr - 10
		Ca - 40	Ti - 10
		Ga - 10	

600 Grit Alundum - (Buehler, Ltd.)

The material was produced by fusing bauxite in an electric furnace, crushing, comminuting and classifying.

Gray in color

Sp Gr	-	3.3 - 3.6
Average particle size	-	17 microns
Crystalline modification	-	predominately (alpha) cubic



Tests Performed. Identical procedures were employed in tests 1 - 16. The alumina to be employed as the disperse phase was first slurried in the electrolyte, then dispersed by mixing in a high speed Waring Blender for ten minutes.

The electrolyte containing the disperse phase was transferred to the electrolytic cell, the time noted and electrolysis begun. A full wave, capacitive filtered, direct current power supply with approximately 15% ripple was employed for all electrolytic experiments. (Voltage and power range of rectifier, 22 V.D.C. 25 amperes)

The agitation employed was just sufficient to keep the disperse in suspension.

Operating conditions for runs 1 - 4 are given below:

Run - 1

Electrolyte -	Copper Formate	
Disperse Phase -	Alon-C	25 grams per liter
Current Density, Anode and Cathode -	30 amperes per square foot	
Cell voltage -	2.30 volts direct current	
Temperature of bath	-	25°C
Deposit wt.	-	22.8 grams <sup>7</sup>
Duration of Test	-	11.7 hours
Deposit Appearance	-	Smooth, with little edge effect

<sup>7</sup>The top and bottom deposits were weighed separately on this test, to ensure that anode and cathode arrangement were such that upper and lower cathode surfaces had the same current density. Top deposit weighed 11.1 grams bottom deposit weighed 11.7 grams. This was considered satisfactory and on subsequent tests only the total deposit weight was measured.

## Run - 2

Electrolyte - Copper Formate

Disperse Phase - Linde B-5125      25 grams per liter

Current Density - Anode and Cathode - 30 amperes per  
square foot

Cell voltage - 2.47 volts direct current

Temperature of bath      -      25°C

Deposit wt.      -      56.5 grams

Duration of Test      -      18.8 hours

Deposit Appearance      -      Smooth with little  
edge effect

## Run - 3

Electrolyte - Copper Formate

Disperse Phase - Linde A-5175      25 grams per liter

Current Density - Anode and Cathode - 30 amperes per  
square foot

Cell voltage - 2.53 volts direct current

Temperature of bath      -      25°C

Deposit wt.      -      51.3 grams

Duration of Test      -      18.2 hours

Deposit Appearance      -      Smooth, slight edge  
effect. Some treeing  
at outer corners of  
cathode

## Run - 4

Electrolyte - Copper Formate

Disperse Phase - 600 grit Alundum      25 grams per liter

Current Density - Anode and Cathode - 30 amperes per  
square foot

Cell voltage - 2.30 volts direct current

Temperature of bath	-	25°C
Deposit wt.	-	53.7 grams
Deposit Appearance	-	Smooth and possessing a grayish cast

Attempts to produce satisfactory deposits in the Copper Sulfate Sulfuric acid bath were unsuccessful because of the very rough and heavily treed cathode deposits obtained.

Run - 7 produced a cathode so heavily treed that the deposit had the appearance of sheep's wool. In Runs 8,9 and 10 various addition agents were used in the bath to improve the cathode deposit. Additions of 50 milligrams/liter Armours bone glue, 1 gram per liter molasses, and 2 grams per liter molasses, common addition agents in copper plating electrolytes, were employed in Runs 8, 9 and 10 respectively. Although cathode appearance improved in each successive test, none of the deposits were satisfactory.

The difficulty was discovered in Run - 11 in which no disperse phase was employed. The cause of the roughness was a heavy anode sludge depositing on the cathode and acting as sites for nodulation.

Cathode appearance in Run - 12 was improved significantly by placing the anode in a nylon twill weave bag; however, the sludge was sufficiently fine to ultimately pass through the anode bag and cause roughness at the cathode.

Substitution of OFHC, (reg. trade) brand copper for the electrolytic cathode copper employed in previous tests in conjunction with

bagging the anode was found to be completely satisfactory for production of smooth cathode deposits.

## Run - 13

Electrolyte - Copper Sulfate, Sulfuric Acid

Disperse Phase - Alon-C 25 grams per liter

Current Density Anode and Cathode - 30 amperes per square foot

Cell voltage - 0.92 volts direct current

Temperature of bath - 25°C

Deposit wt. - 83.0 grams

Duration of Test - 29.7 hours

Deposit appearance - Good with slight nodulation

## Run - 14

Electrolyte - Copper Sulfate, Sulfuric Acid

Disperse Phase - Linde B-5125 25 grams per liter

Current Density - Anode and Cathode - 30 amperes per square foot

Cell voltage 0.97 volts direct current

Temperature of bath - 25°C

Deposit wt. - 34.0 grams

Duration of Test - 12.6 hours

Deposit Appearance - Excellent, Cathode surface extremely smooth, completely free of nodulation

## Run - 15

Electrolyte - Copper Sulfate, Sulfuric Acid

Disperse Phase - Linde A-5175 25 grams per liter

Current Density - Anode and Cathode - 30 amperes per  
square foot

Cell voltage 0.95 volts direct current

Temperature of bath	-	25°C
Deposit wt.	-	52.0 grams
Duration of Test	-	20.1 hours
Deposit Appearance	-	Good, slight nodulation

Run - 16

Electrolyte - Copper Sulfate, Sulfuric Acid

Disperse Phase - 600 grit Alundum 25 grams per liter

Current Density - Anode and Cathode - 30 amperes per  
square foot

Cell voltage 0.92 volts direct current

Temperature of bath	-	25°C
Deposit wt.	-	50.0 grams
Duration of Test	-	20.1 hours
Deposit appearance	-	Good, slight nodulation, treeing

At the conclusion of the electrodeposition experiments the deposits were mechanically stripped from the cathodes. This was easily accomplished because electrodeposited copper forms a very weakly adherent bond to stainless steel.

The edges of the deposit were trimmed off with shears, the deposits were thoroughly washed to remove any electrolyte, and analyzed for alumina.

### Analytical Procedure

The total deposit, exclusive of the trimmed edges was accurately weighed and dissolved in concentrated nitric acid. The aluminas studied are substantially insoluble in nitric acid.

After dissolution with nitric acid the slurry of alumina in nitric acid was adjusted with concentrated ammonia to a pH between 7 and 8.

The slurry was filtered by gravity through Whatman 42 ashless paper, and washed with a 10 volume percent boiling aqueous ammonia solution to free the residue of copper salts.

After a final water wash the residue and filter paper were transferred to a tared porcelain crucible and ashed to constant weight.

The weight of the residue after firing was taken as alumina.

The results of the deposition tests are tabulated below:

## TABULATION OF RESULTS

Analyses of Cathode Deposits obtained in Copper

Formate Electrolytic Bath

Table - 1

Disperse Phase	Conc. in Electrolyte grams per litter	Wt % $Al_2O_3$ in Cathode Deposit		Average Particle D Milli- microns	Wt Ratio $Al_2O_3$	
		Cathode Top	Cathode Bottom		Top to	Bottom
Alon-C	25	0.089	0.029	30	3.1	
Linde B- 5125	25	2.11	1.20	50	1.76	
Linde A- 5175	25	5.16	2.15	300	2.4	
600 grit Alundum	25	13.2	2.88	17000	4.6	

## Analyses of Cathode Deposits obtained in Copper

## Sulfate Sulfuric Acid Electrolyte

Table - 2

Disperse Phase	Conc. in Electrolyte grams per liter	Wt % $Al_2O_3$ in Cathode Deposit		Average Particle D Milli- microns	Wt Ratio $Al_2O_3$	
		Cathode Top	Cathode Bottom		Top to	Bottom
Alon-C	25	0.20	0.026	30	7.7	
Linde B- 5125	25	0.020	0.042	50	.48	
Linde A	25	0.63	0.029	300	2.2	
600 grit Alundum	25	0.15	0.021	17000	7.1	

Considerably more confidence may be placed in the accuracy of the % of Linde-B, Linde A, and 600 grit alundum in the copper deposits obtained in the formate baths than in the other alumina analyses.

Analyses of Alon-C and of all the aluminas reported in the deposits obtained in the acid sulfate bath should be interpreted as indicative of a trend rather than a definitive measure of deposit content. Due to the low percentages of  $Al_2O_3$  in the deposits a small weighing error could cause a substantial change in the reported analysis.



## Ratio of Deposit Content Formate to

## Sulfate Bath

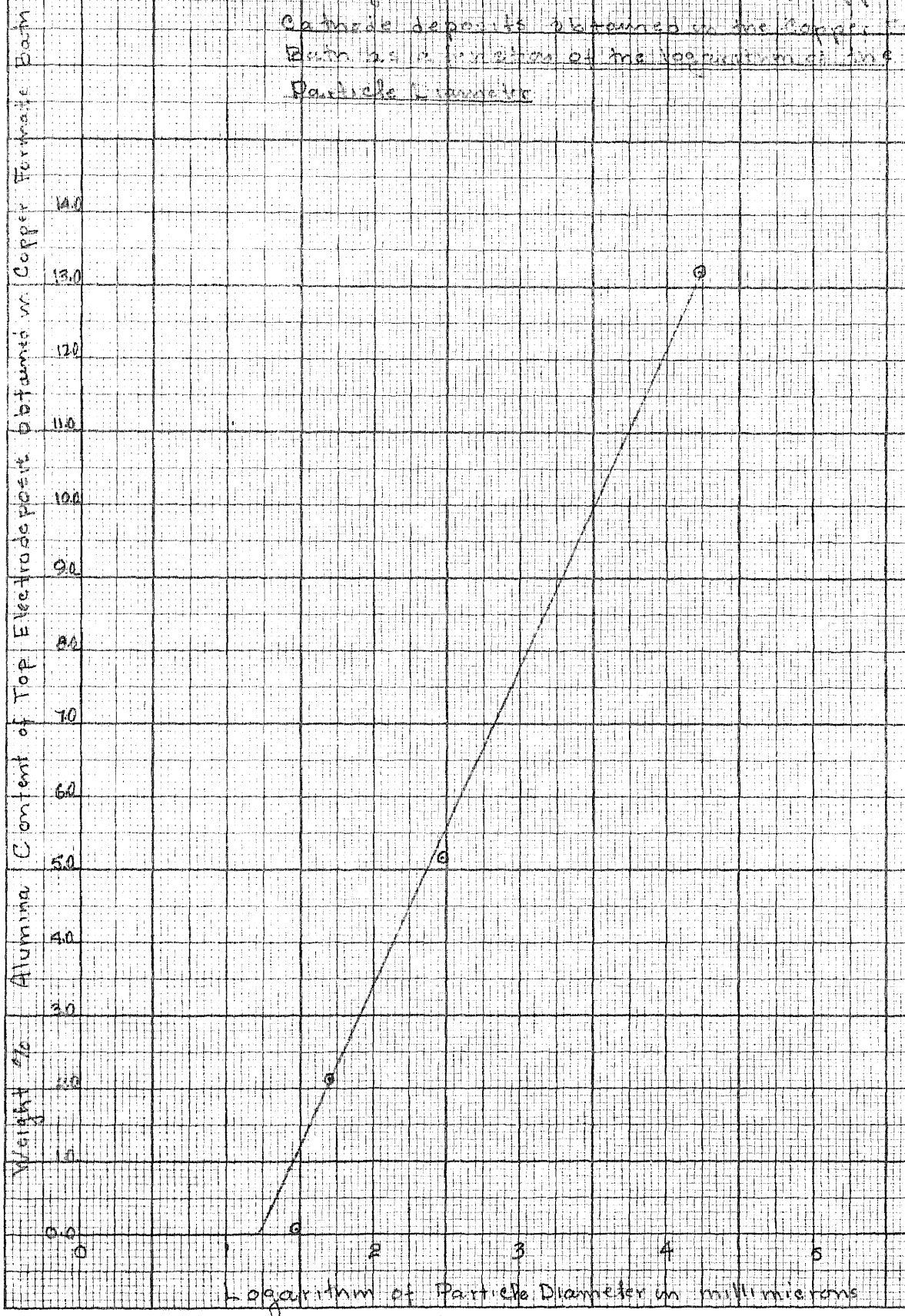
Table - 3

Disperse Phase	Ratio of	$\frac{\text{Wt } \% \text{ Al}_2\text{O}_3 \text{ in Copper Formate Deposits}}{\text{Wt } \% \text{ Al}_2\text{O}_3 \text{ in Acid Copper Sulfate Deposits}}$	
		Top Deposits	Bottom Deposits
Alon-C	.45		1.1
Linde B-5125	106		29
Linde A-5175	82		74
600 grit Alundum	88		136
<hr/>			
Average	69		60
<hr/>			

The same caution must be applied here in interpreting results as was mentioned previously.

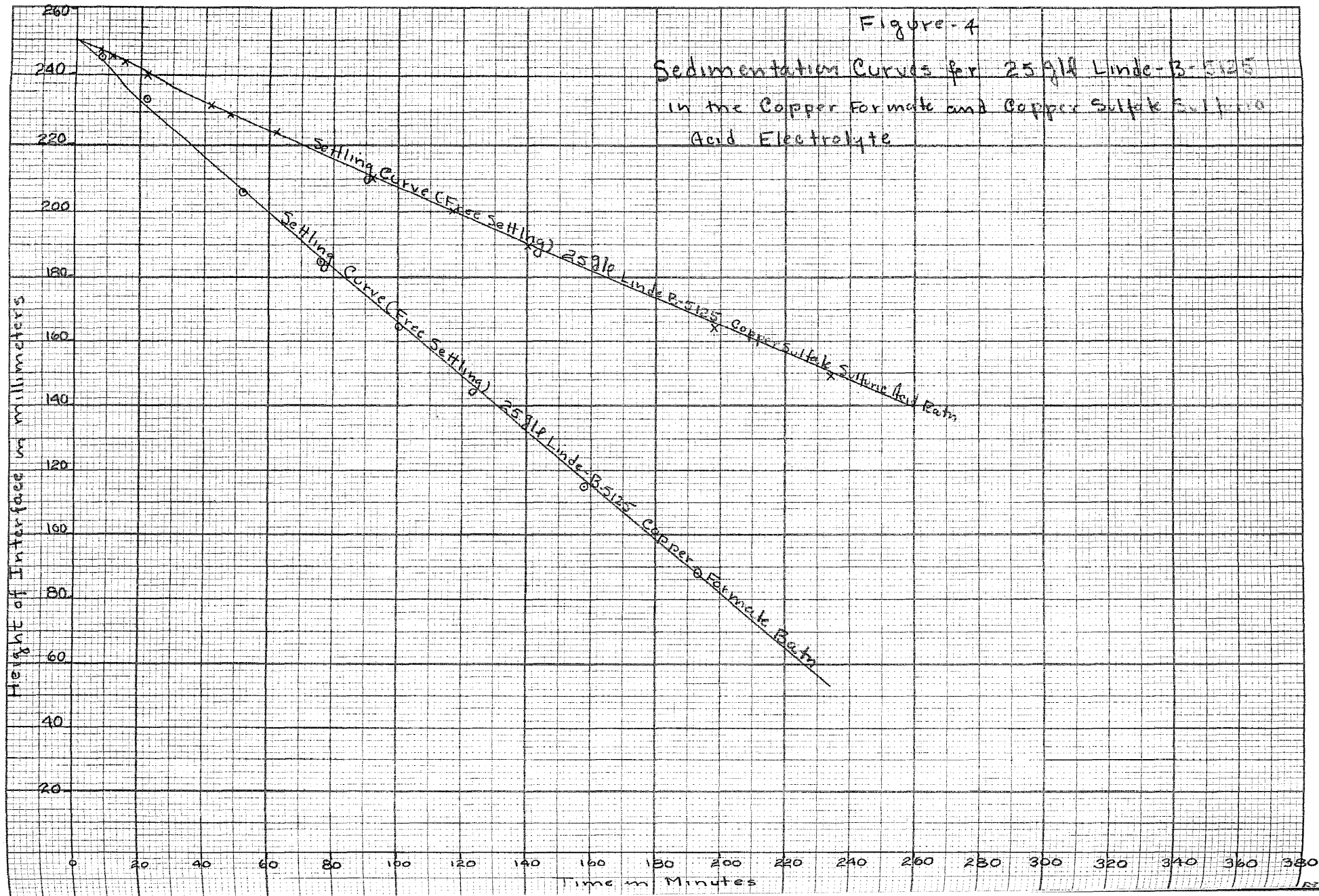
Figure 3

Weight Percent Al<sub>2</sub>O<sub>3</sub> content of Upper Cathodic deposits obtained in the Copper Ferrate Bath as a function of the logarithm of the Particle Diameter



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### Evaluation of Data and Conclusions

It was stated previously in the text of this paper that three conditions had to be satisfied in order that mechanical inclusion be the controlling mechanism whereby aluminas are co-deposited with copper during electrodeposition of copper.

The first condition, that the content of  $\text{Al}_2\text{O}_3$  in the deposit should increase with particle size is satisfied. Reference to Tables 1 and 2 indicate that as particle size of the disperse phase is increased the content of the co-deposited alumina also increases.

A plot of the logarithm of particle diameter against the alumina content for horizontal cathodes facing the direction of falling particles in the copper formate bath is illustrated in Figure (3).

By fitting the curve to the slope intercept equation one obtains the following relationship for the alumina content as a function of particle size;

$$\% \text{Al}_2\text{O}_3 \text{ (in deposit)} = 4.38 \log.D - 5.35$$

where D is the particle diameter of the disperse phase in millimicrons. The equation is valid only over the range of particle sizes studied.

The second condition, that the disposition of the cathode surfaces relative to the direction of the falling particles constituting the disperse phase should effect the alumina content of the electrodeposit is satisfied. Reference to Tables 1 and 2 indicate that in seven of the eight experiments performed the ratio of the alumina content of the top electrodeposit to the bottom electrodeposit was sub-

stantially greater than one. Those analyses in which the most confidence may be placed indicate also, as would be anticipated, that the ratio of the  $\text{Al}_2\text{O}_3$  content of the upper cathode to the lower cathode increases as a function of particle size.

Condition three, that in systems of identical geometry the deposit content should be independent of the bath composition is definitely not satisfied.

The possibility of bath density or viscosity may be discounted by reference to Figure (4). Though admittedly a difference of approximately a factor of two (2) exists in the sedimentation rate of the copper formate and copper sulfate, sulfuric acid baths this is inadequate to account for a difference of a factor of 67 in the wt % of alumina in the cathodes obtained.

Another interesting observation concerns the average ratio of the alumina contents of the top and bottom cathodes of the copper formate bath to the alumina content of the top and bottom cathodes in the copper sulfate sulfuric acid bath, tending to indicate a relationship between alumina content and bath compositions.

In summation it may be concluded that within a particular bath composition the phenomenon of mechanical inclusion effects the alumina content of the deposit, but is in itself controlled by the nature of the electrolyte employed.

## CHAPTER II

### CONSIDERATION OF ELECTROPHORETIC MIGRATION AS THE CONTROLLING MECHANISM FOR THE CO-DEPOSITION OF ALUMINA WITH COPPER DURING ELECTRO DEPOSITION OF COPPER

#### Introduction:

Electrophoresis may be defined as the migration of charged particles, suspended<sup>8</sup> in a solution, under the influence of an electric field.

In consideration of the co-deposition of aluminas with copper by electrophoresis, the phenomenon may be thought of as the electric field surrounding the cathode exerting an electrostatic force of attraction on the alumina particle. The electrostatic force of attraction would cause the particle to migrate to the cathode and be bound there.

Once bound to the cathode the particle would become embedded in the matrix of copper deposited over it.

Theoretical considerations, which will be discussed in greater detail below, indicate that the zeta potential of the disperse phase will determine whether or not a particle may be electrophoretically deposited.

<sup>8</sup> The choice of the word suspended is unfortunate, since it allows the inference that ions and molecules, are excluded from exhibiting electrophoretic effects. Migration of complex ions is sometimes referred to as ionophoresis. The term electrophoresis is completely applicable to migration of macro-molecules in an electric field.

The derivation of the zeta potential offered below relies on several references,<sup>9,10,11,12</sup>

Diagrammatic Representation of the

Double Layer

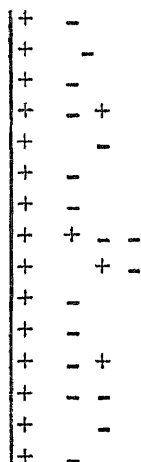


Fig. (5)

The concept of the zeta potential is based on the idea of an electrical double layer, occurring at the interface between a liquid and a solid. In Fig. (5) the black line indicates a fixed solid sur-

- <sup>9</sup> Perrin J., J. Chim. Phys. 2 607 (1904)
- <sup>10</sup> Bier Milan - Electrophoresis, Theory Methods and Applications Academic Press, Inc. 1959
- <sup>11</sup> Glasstone Samuel - An Introduction to Electro-Chemistry. D. Van Nostrand Co., Inc. 1942
- <sup>12</sup> Butler J. A. V. Electrical Phenomena at Interfaces The Mac Millan Co. New York, 1951

face while the positive charges represent strongly adsorbed molecules or ions constituting the fixed portion of the double layer. The charges some distance away from the fixed charges represent the diffuse component of the double layer. The system is clearly analogous to a parallel plate condenser. According to the laws of electrostatics

$$V = \frac{4\pi e t}{D}$$

where  $V$  represents the potential difference between the diffuse and fixed charge layers

$e$  - represent the charge density

$t$  - the distance between plates

$D$  - the dielectric constant of the medium

$\pi$  - constant - 3.1414

If the double layer is equivalent to a parallel plate condenser then the zeta potential may be written as

$$\zeta = \frac{4\pi\sigma d}{D}$$

where  $\sigma$  represents the charge density

$d$  - the thickness of the double layer

$D$  - the dielectric constant of the medium

To prove the relationship is correct consider an element of volume, at an infinite distance from the fixed portion of the double layer whose time average potential is  $\psi$ .

Work required to bring an ion from infinity into the double layer would be



$$\begin{aligned} Z e \psi & \quad - \quad \text{for a positive ion} \\ -Z e \psi & \quad - \quad \text{for a negative ion} \end{aligned}$$

Applying the Boltzmann Distribution law to ions to determine the time average number of positive and negative ions yields

$$\frac{dn}{dv} = n_+ \exp\left(-\frac{Z_+ e \psi}{kT}\right)$$

$$\frac{dn}{dv} = n_- \exp\left(-\frac{Z_- e \psi}{kT}\right)$$

where  $n_+$ ,  $n_-$  represent the total numbers of positive and negative ions respectively in a unit volume.

The net charge or charge density per unit volume then becomes

$$\rho = e \left( n_+ Z_+ \exp\left(-\frac{Z_+ e \psi}{kT}\right) - n_- Z_- \exp\left(-\frac{Z_- e \psi}{kT}\right) \right)$$

If the assumption is made that  $\frac{Z e \psi}{kT}$  is much less than unity

then  $\exp\left(-\frac{Z_+ e \psi}{kT}\right)$  and  $\exp\left(-\frac{Z_- e \psi}{kT}\right)$  may be expressed as a power series

yielding  $\rho = -\frac{e^2 \psi}{kT} \sum_i n_i Z_i^2$ , in order to solve for

time average of potential, it is necessary to have another equation relating  $\rho$  and  $\psi$

The second relationship relies on the fact that the potential  $\psi$  and the electrical charge density  $\rho$  may be related by Poisson's equation.

Poisson's equation in rectangular coordinates takes the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi \rho}{D}$$

Since the particle diameter of the aluminas studied is very much greater than the thickness of the double layer the surface of the particle will be considered infinite in extent in the Y and Z directions, that is the electric potential will vary only in the X direction, normal to the surface of the particle.

$$\text{Then } \frac{\partial^2 \Psi}{\partial Y^2} = 0$$

$$\frac{\partial^2 \Psi}{\partial Z^2} = 0$$

And the final form of the equation is

$$\frac{d^2 \Psi}{dx^2} = - \frac{4\pi p}{D}$$

$$\frac{d^2 \Psi}{dx^2} = + \frac{4\pi}{D} \left( \frac{E^2 \Psi \sum n_i \bar{z}_i^2}{KT} \right)$$

$$\text{let } \left[ \frac{4\pi}{D} \left( \frac{E^2}{KT} \sum_i n_i \bar{z}_i^2 \right) \right]^{\frac{1}{2}} = K$$

This can be simplified appreciably by combining constants.

$$= 4.802 \times 10^{-10} \text{ e.s. units}$$

$$k = (\text{gas constant per molecule}) - 1.38 \times 10^{-16}$$

$n_i$  = no. of each ion per cubic centimeters obtained  
by multiplying concentration in gram moles per  
liter (Ci) by  $6.02 \times 10^{20}$

Substituting in constants yields

$$K = \left[ \frac{(4)(3.14)(6.02 \times 10^{20})(4.802)^2 \times 10^{-20}}{1.38 \times 10^{-16} DT} \sum_i C_i \bar{z}_i^2 \right]^{\frac{1}{2}}$$

$$\text{or } \frac{1}{K} = 2.81 \times 10^{-10} \left[ \frac{DT}{\sum_i C_i \bar{z}_i^2} \right]^{\frac{1}{2}}$$

Making substitution

$$\frac{d^2 \Psi}{dx^2} = \Psi K^2$$

The solution of this equation takes the form

$$\psi = C_1 e^{-kx} + C_2 e^{kx}$$

evaluating constants as  $x \longrightarrow \infty$

$$\psi \longrightarrow 0$$

Therefore  $C_2$  must be equal to zero

and  $\psi = C e^{-kx}$

Now since  $\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi\rho}{D}$

and  $\frac{\partial^2 \psi}{\partial x^2} = k^2 \psi$

$$k^2 \psi = -\frac{4\pi\rho}{D}$$

Substituting

$$k^2 C e^{-kx} = -\frac{4\pi\rho}{D k^2} \quad \rho = \frac{CDk^2 e^{-kx}}{4\pi}$$

Since  $\rho$  represents charge density at any point in the solution, and further since the charge  $\sigma$  on the fixed component of the double layer, in our case the alumina particle, must be equal in magnitude to the total charge in the diffuse layer; the net charge on the fixed component of the double layer may be determined by a summation of the charge density in the diffuse layer from the fixed double layer to infinity.

$$\sigma = - \int_a^{\infty} \rho dx$$

where (a) is the distance of closest approach of the diffuse layer to the fixed layer

$$\sigma = - \int_a^{\infty} \frac{CDk^2 e^{-kx}}{4\pi} dx$$

$$\sigma = \frac{C D K^2}{4\pi} \int_a^{\infty} e^{-Kx} dx$$

Therefore 
$$C = \frac{4\pi\sigma}{D K} e^{Ka}$$

It is assumed in this integration that  $K$  is a constant, i.e. the concentration and species of ions in the double layer is identical with that in the bulk of the solution. This may not be the case, but no evidence to contravert it could be located in the literature.

Continuing: The value of the constant  $C_1$  may now be substituted in the expression for electrical potential as a function of distance.

$$\psi = \left( \frac{4\pi\sigma}{D K} \right) (e^{Ka}) (e^{-Kx})$$

$$\psi = \left( \frac{4\pi\sigma}{D K} \right) (e^{K(a-x)})$$

if  $K$  is small then  $e^{K(a-x)}$  is approximately equal to 1 and the equation reduces to 
$$\psi = \frac{4\pi\sigma}{D K}$$

yielding an equation

equivalent to 
$$\psi = \frac{4\pi\sigma d}{D}$$

where  $d = \frac{1}{K}$  represents the thickness of the double layer, by analogy the distance between condenser plates.

Illustrative calculations are offered below for  $K$  in the copper formate, and copper sulfate sulfuric acid baths.

As defined previously  $\frac{1}{K} = 2.8 \times 10^{-10} \left[ \frac{DT}{\sum_i C_i z_i^2} \right]^{\frac{1}{2}}$

An assumed value of D will be used since no values for aqueous solutions were located in the literature

$$D = 10$$

$$T = 298^\circ\text{K}$$

for the Copper Formate Bath

Table - 4

Calculation of  $C_i z_i^2$  for Copper Formate Bath

Constituent	$C_i$	$z_i^2$	$C_i z_i^2$
$\text{NH}_4$	.477	1	.477
OOCH	.477	1	.477
Cu	.803	4	3.212
K	.344	1	.344
$\text{SO}_4$	.975	4	3.900

$$\sum_i C_i z_i^2 = 8.410$$

$$\frac{1}{K} = (2.81 \times 10^{-10}) \left( \frac{(298)(10)}{8.41} \right)^{1/2}$$

$$\frac{1}{K} = (2.81 \times 10^{-10}) (18.8) = 52.9 \times 10^{-10}$$

$$\frac{1}{K} = .529 \times 10^{-8} = .529 \text{ A}^\circ$$

$$K = 1.89 \times 10^8 \text{ centimeters}^{-1}$$

Similar calculations for the Copper Sulfate Sulfuric acid bath  
yield

$$\frac{1}{K} = 47.2 \times 10^{-10} \text{ centimeters} = .472 \text{ A}^\circ$$

In order to obtain some qualitative indication of the magnitude of the zeta potential at  $\frac{1}{K} = .529, .472A^0$  experimental data for the zeta potential of aqueous solution of barium chloride with glass<sup>12a</sup> as a function of barium chloride concentration was obtained. The thickness of the double layer was calculated, assuming a dielectric constant (D) of 50.

The zeta potential of the barium chloride, glass system was plotted as a function of thickness of the double layer and values for the double layer thickness of the two copper plating baths studied were added to the graph. See Fig. (6)

It may be seen from Fig. (6) that the value of the zeta potential for the System barium chloride, glass approaches zero at concentrations considerably more dilute than those employed in the copper plating baths.

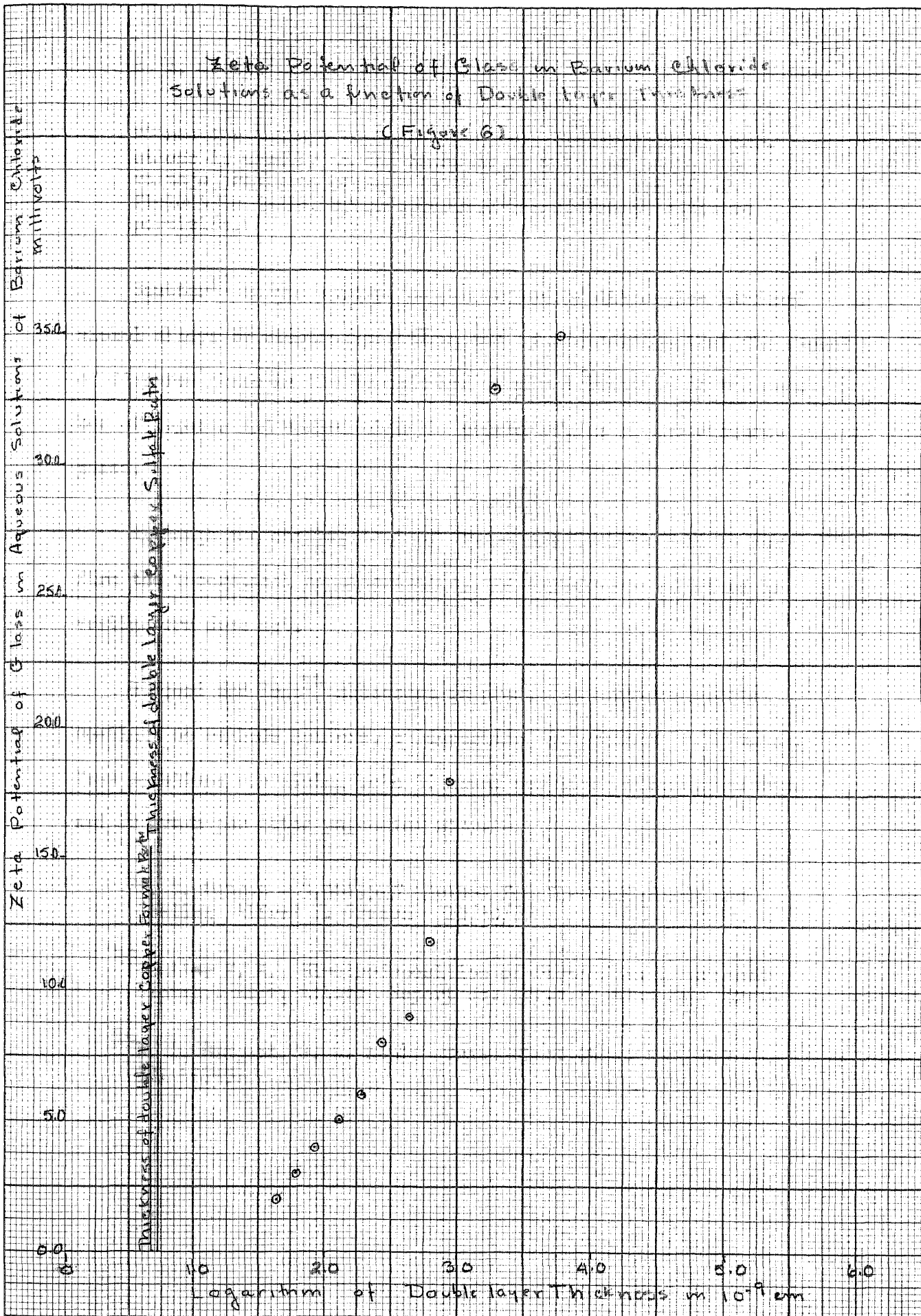
If comparison between systems of strong electrolytes is valid, then a zeta potential very close to zero may be anticipated in the copper plating baths studied.

#### Practical Considerations of Electrophoretic Deposition in High Conductivity Systems

If theoretical considerations concerning the possibility of electrophoretic effects in high conductivity electrolytes were consistently substantiated by actual experiment one could definitively state that electrophoresis plays no part in the co-deposition of aluminas with copper.

<sup>12a</sup> A. J. Ham E. D. M. Dean Trans. Far Soc - 36  
1-322 (1940) pp 55

Zeta Potential of Glass in Barium Chloride Solutions as a function of Double layer thickness (Figure 6)



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Thickness of Double Layer Copper Formate Part

A. E. Grazen<sup>4</sup> makes the statement

"Since the voltage employed in normal electroplating operations is usually in the order of 12 volts or less, the voltage gradients present in the electrolyte are insufficient to cause any cataphoretic deposition of additive particles."

Sautter<sup>13</sup> in his studies on production of dispersion hardened nickel alloys by electrodeposition, was of the opinion that the amount of disperse phase in the deposit was simply a function of the number of impacts and varied with the concentration of the disperse phase.

Although the observations of Grazen and Sautter tend to confirm the theoretical considerations, the experiences of other investigators does not.

Bidgood and Kent<sup>14</sup> succeeded in producing electrophoretic coatings on cathode heaters, at deposition potentials of 30 volts, from solutions containing both 30 grams per liter aluminum nitrate and 20 grams per liter magnesium nitrate.

<sup>4</sup>U. S. Patent - 3,061,525 Method for Electroforming and Coating Alfred E. Grazen 10/30/67

<sup>13</sup>Sautter F. K. Electrodeposition of Dispersion - Hardened Nickel - Al<sub>2</sub>O<sub>3</sub> Alloys Report No. WVT-R.R. 6204 Feb. 62

<sup>14</sup>E. S. Bidgood, G. H. Kent Trans Elec. Chem. Soc. 8.7 321 (1945)



Williams and Martin<sup>15</sup> in their studies on electrodeposited composite coatings make the statement

"It is possible that the fibers or particles are transferred to the cathode by electrophoretic action to be keyed into the matrix by the electrolytic deposition of the matrix metal."

and later in the same paper state

"In view of the sensitivity of success of the co-deposition technique on the hydrogen ion concentration in the bath, it would appear that electrophoresis plays a significant part in the process."

The baths studied and employed successfully for production of electrodeposited composite coatings included a sulfuric acid, copper sulfate bath very comparable to the one employed in the present studies.

Actual measurements of what purported to be the zeta potential were made by Khan and Sosnovskii<sup>16</sup> on lead dioxide particles in solutions 0.3 to 1.0 molar in sulfuric acid and .18 to .85 molar in cadmium.

Their measurements, made by the ultramicroscope technique, indicated that the lead dioxide particles possessed a zeta potential of 47.5 millivolts.

<sup>15</sup> R. V. Williams and P. W. Martin - Electrodeposited Composite Coatings. British Iron and Steel Research Association, London, S W 11 (1964)

<sup>16</sup> Khan O. A. and Sosnovskii G. N. Cataphoretic Transfer of PbO<sub>2</sub> Particles in Solutions Containing H<sub>2</sub>SO<sub>4</sub> and CdSO<sub>4</sub>. Zh. Prikl Khim 37 (4) 890-2 (1964)

Electrophoretic Measurements. Measurements of the zeta potential of the various aluminas were first attempted in distilled water.

The method employed for measurement of zeta potential, was the moving boundary technique.<sup>17</sup>

Use of the moving boundary technique involves measuring the velocity, in an electric field, of the boundary formed between a suspension of the disperse phase, and the suspending medium.

From the velocity of the boundary, the potential gradient employed and the dielectric constant and viscosity of the system studied the zeta potential of the disperse phase may be calculated.

Moving boundary measurements were made in a Burton U-tube, see Fig. (7). This method possesses the advantage of requiring no elaborate voltage measuring equipment and is capable of producing results reproducible within five per cent.

Prior to any test work the U-tube was allowed to stand in aqua regia over night to insure its absolute cleanliness.

The procedure employed in filling the U-tube was to first introduce the supporting electrolyte<sup>18</sup> into the U-tube from the top by removing an electrode until partially filled, then very carefully and

<sup>17</sup> Bikerman J. J. Trans Far Soc - 32 1648-52 (1936)

<sup>18</sup> The supporting electrolyte is simply a liquid of the same composition as that in which the disperse phase is suspended; however, the supporting electrolyte has no disperse phase.

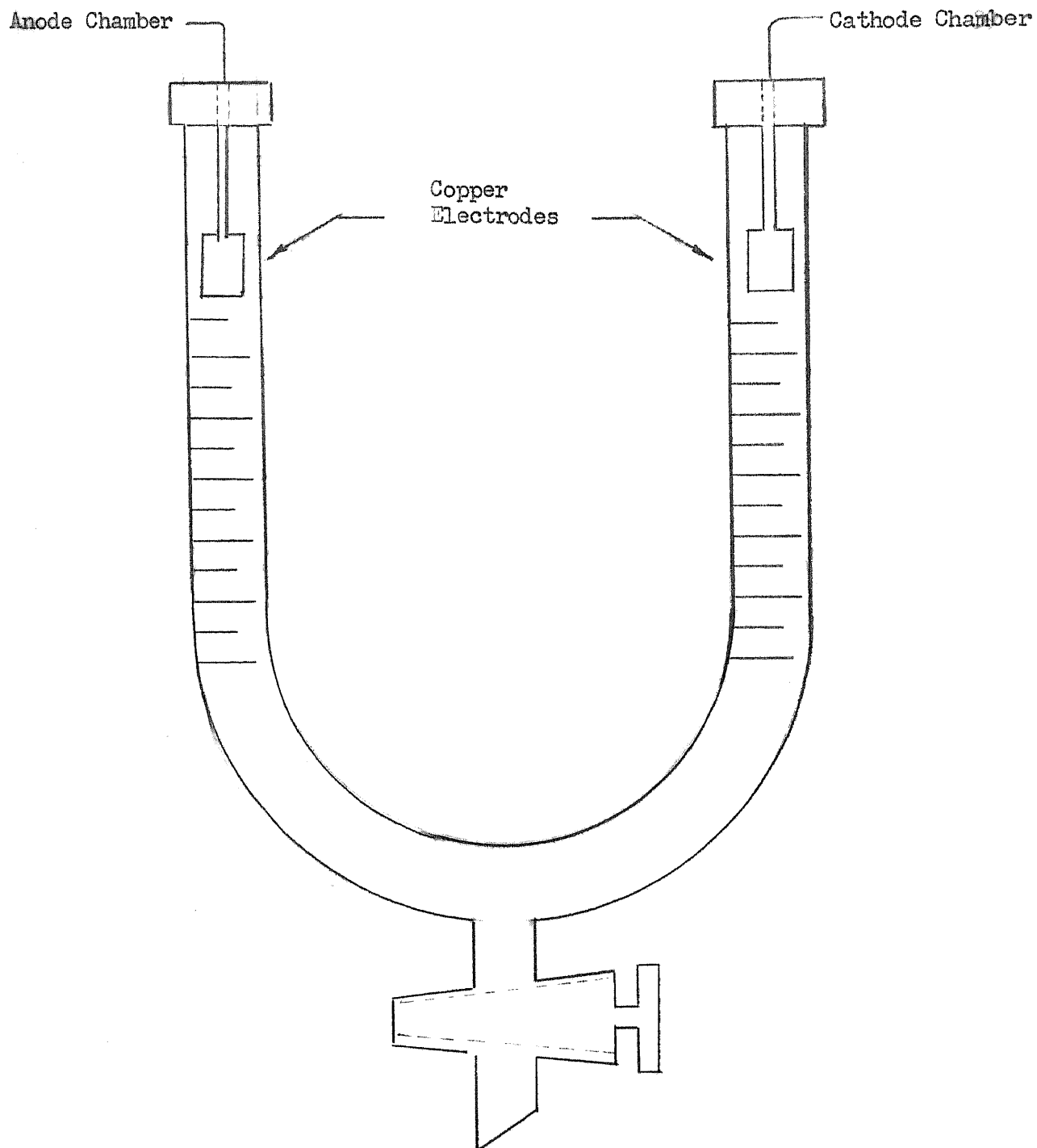


Fig. (7)

Burton U-Tube Apparatus  
for Moving Boundary Measurements

slowly introduce the suspension through the bottom stopcock. If properly done a sharp boundary will form between the disperse phase and the supporting electrolyte.

When the supporting electrolyte had covered the electrodes, the stopcock was closed.

To measure the mobility of the disperse phase the power was applied, and the voltage increased until a noticeable rate of boundary movement was attained.

The voltage required and the boundary velocity were noted. Data obtained for Alon-C is tabulated below.

## TABULATION OF RESULTS

## U-Tube Measurements

## Disperse Phase - Alon-C

## Supporting Electrolyte - Water

Table - 5

## Moving Boundary Data for Alon-C

Time min.	Voltage Volts D.C.	Height of Inter- face millimeters Anode Leg	Current milliamperes
0	0.0	20	0.0
2	610	16	1.35
5	610	11	1.60
8	615	5	1.65
10	615	1	1.65

Similar readings may be obtained by reading the increase in the height of interface in the cathode chamber.

## Calculation of the zeta potential

Length of U-tube - 30 centimeters

Voltage gradient -  $612 \times 1/30 = 20.4 \frac{\text{volts}}{\text{centimeters}}$

$\mu$  - mobility =  $\frac{1.90 \text{ cm}}{10 \times 60} = .00317 = 3.17 \times 10^{-3} \frac{\text{cm}}{\text{sec.}}$

D - dielectric constant - 80

$\eta$  - viscosity of medium - 0.010 poise

$$\zeta = \frac{4\pi\eta\mu}{D} \times 9 \times 10^4 \text{ volts }^{19}$$

<sup>19</sup> See Potter E. C. "Electrochemistry" p 173

where  $- 9 \times 10^4$  - is the conversion factor for electrostatic units <sup>41</sup>  
to volts

Substituting

$$\zeta = \frac{(4)(3.14)(1 \times 10^{-2})(3.17 \times 10^{-3})(9 \times 10^4)}{80}$$

$$\zeta = .448 \text{ volts} = 448 \text{ millivolts}$$

The sign of the charge is determined by the direction of the moving boundary. Since the boundary rose toward the cathode, negatively charged, the particles possess a positive charge. Therefore

$$\zeta = + 448 \text{ millivolts}$$

Attempts to measure the zeta potential of the other aluminas in distilled water were unsuccessful. The size of the particles was too great for a stable suspension to form.

Zeta potential determinations were also attempted on Alon-C suspended in the copper sulfate sulfuric acid bath at various concentrations. The conditions of the tests are tabulated below.

## Variables Studied; Moving Boundary Method;

## Alon-C in Copper Sulfate Bath

Table - 6

Bath	Conc	Voltage V.D.C.	Boundary Velocity
CuSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	Normal	20	None
" "	Dil 10:1	57,111,160	None
" "	Dil 100:1	225,428	None
CuSO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> 100 mg/l Thiourea	Normal	19.3	None
" "	Dil 10:1	60,110,161	None
" "	Dil 100:1	225,450	None

Despite the variety of concentrations and voltages employed in the measurements, no discernible, boundary motion could be detected; in fact the suspensions prepared at dilute concentrations of electrolyte, 10:1, 100:1, were less stable than that of suspensions prepared with undiluted electrolyte.

## Experimental Procedure Part II

### Coulometer Studies.

#### Introduction:

Since no definitive results were obtained from attempts to measure the zeta potential of aluminas directly, studies were taken to determine if a portion of the deposition current was carried by the disperse phase.

It was reasoned that if the particles acted as charge carriers for the deposition current, the copper deposited would be less than the theoretical amount; since a portion of the current ordinarily carried by copper ions would be carried by the disperse phase.

It was anticipated that the portion of the deposition current carried by the disperse phase would be quite small and attempts to determine it would require a highly accurate measure of the total current passed. This necessitated the use of a coulometer.

In order to enhance the portion of the current carried by the disperse phase, the aluminas employed were those which produced electrodeposits with the highest disperse phase content. To further enhance the quantity of alumina in the electrodeposit, a cell identical in all respects to that employed in the studies of mechanical inclusion was used. The anodes were the same as used in the previous studies. The bottom surface of the cathode was masked with electroplaters tape so as to obtain deposition only on the upper surface.

Description of Equipment. The coulometer employed consisted of two anodes of identical dimensions, cut from cast OFHC, (reg. trade)



copper. The cathode was equal in area to the effective anode area and was situated equidistant from the anode and in a plane parallel to the plane of the anodes.

The electrolyte employed in the coulometer was similar to that recommended by the National Bureau of Standards. The composition was:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	-	200 grams per liter
$\text{H}_2\text{SO}_4$	-	5 grams per liter
Ethanol	-	3 milliliters per liter

The coulometer was placed electrically in series with the two deposition cells, tank-1 and tank-2, whose compositions are given below:

Tank - 1

Standard Copper Formate Bath

Disperse phase - Linde A - 25 grams per liter

Tank - 2

Standard Copper Formate Bath

Disperse phase - 600 grit Alundum - 25 grams  
per liter

The cathodes employed in the coulometer and the deposition tanks were carefully cleaned, accurately weighed and positioned in their respective tanks.

The tanks were charged with electrolyte and electrolysis started immediately. At the completion of the run, the cathodes were removed

from the tanks, washed copiously with distilled water, dried at 80°C and weighed.

The deposits containing the disperse phase were stripped from the cathode mechanically and analyzed for alumina. The results are given below:

#### TABULATION OF RESULTS

Coulometer Cathode Weight initially	-	56.4140 grams
Coulometer Cathode Weight after Electrolysis	-	82.4389 "
Weight of Copper deposited in coulometer	-	26.0249 "
Weight of Cathode deposit stripped	-	26.0242 "
Weight of Cathode 1 initially	-	106.0773
Weight of Cathode 1 after Electrolysis	-	134.2860
Weight of Cathode deposit	-	28.2087
Weight of Cathode deposit stripped	-	28.0783 <sup>20</sup>
Weight of Cathode 2 initially	-	101.3700
Weight of Cathode 2 after Electrolysis	-	130.0491
Weight of Cathode deposit	-	28.6791
Weight of Cathode deposit stripped	-	28.6473 <sup>20</sup>

Material reporting in cathode by means other than electro deposition:

$$\text{Tank - 1} \quad 28.0783 - 26.0242 = 2.0541 \text{ grams}$$

$$\text{Tank - 2} \quad 28.6473 - 26.0242 = 2.6231 \text{ grams}$$

<sup>20</sup> The stripped deposit weight is the correct weight. The deposit had not been dried adequately and moisture could be detected between the substrate and the deposit.

Weight of Alumina in Deposit 1 - 1.1629 grams

Weight of Alumina in Deposit 2 - 2.3262 grams

Comparison of the weight of alumina deposited with the material reporting in the cathode by means other than electrodeposition, indicated that the cathodes in Tanks 1 and 2 were operating at greater than 100% current efficiency.

To check this observation the filtrates obtained during the analytical separation of the soluble copper from the alumina, were analyzed for copper electrogravimetrically

Total copper in cathode Deposit - 1    26.446

Total copper in cathode Deposit - 2    26.069

Copper in excess of theoretical for a divalent copper plating bath:

Cathode - 1                    -                    0.422 grams

Cathode - 2                    -                    0.045 grams

An interesting observation was the fact that something other than alumina or copper was present in both deposits, since the sum of the disperse phase and the cathode copper was less than the deposit weight

Cathode - 1    - Deposit Weight    - 28.078

Copper plus alumina - 27.609

Cathode - 2    - Deposit Weight    - 28.647

Copper plus alumina - 28.395

Weight of material other than copper or alumina in cathode deposits

Cathode - 1	-	0.469 grams
Cathode - 2	-	0.252 grams

No attempts were made to identify the unaccounted for material in the cathode.

Two possibilities were considered as capable of causing the deposition of copper in excess of the theoretical amount. The first was the possibility of cuprous ions in the copper formate bath discharging at the cathode. The second possibility was copper entering the deposit as copper ions adsorbed on the alumina particles.

To determine which of the mechanisms conjectured was correct, two copper formate coulometers identical in construction and electrolyte composition were placed in series with the copper sulphate coulometer and electrolyzed for twenty hours.

It was hypothesized that if the first mechanism, monovalent copper ions discharging, was responsible for cathode efficiency greater than 100%, then both cathode deposits obtained in the copper formate bath would be greater in weight than the copper sulfate coulometer deposit by an equal amount.

If adsorbed copper ions on the alumina particles were responsible for a cathode efficiency greater than 100%, then the copper formate

coulometer deposits would be equal in weight to the copper sulfate coulometer deposits. The results are given below:

Copper deposited copper sulfate coulometer -	29.1694 grams
Copper deposited, first copper formate coulometer -	30.8657 grams
Copper deposited, second copper formate coulometer -	30.4891 grams

It is apparent from the data above that neither of the proposed mechanisms was responsible for the excess copper deposited.

Examination of the copper formate coulometer cells revealed the presence of a large amount of anode sludge. Microscopic investigation of copper formate coulometer deposits demonstrated the presence of this sludge in the cathode.

The presence of anode sludge in the cathode deposits vitiated the significance of the test findings and coulometer studies were abandoned.

Experimental Procedure Part IIIInvestigation of Alumina Content of Deposit as a Function of the pH of the Plating Bath.Introduction:

Colloidal substances frequently possess an isoelectric point. The isoelectric point of a substance may be defined as that pH at which an equal number of strongly adsorbed groups of opposite charge are present on the surface of the particle.

At the isoelectric point of a colloidal particle the zeta potential falls to zero.

If the supposition is made that in order to co-deposit electro-phoretically the alumina particle studied must be positively charged, a sharp decrease in the alumina content of the deposit would be anticipated at the isoelectric point of the aluminas.

Previous investigations <sup>1,15,21</sup> have determined that alumina may be co-deposited during the electrodeposition of copper at pH's from 3.5 to 12; while attempts to co-deposit aluminas at pH - 0.5 were unsuccessful. If an isoelectric point exists it is apparent that it must be sought between a pH of 3.5 and 0.5.

<sup>1</sup>Final Report to International Copper Research Assn. Electrodeposition of Dispersion hardened Alloys, Opie W. R. Ernst, R. G., Hoffmann, J. E. May 1, 1964

<sup>15</sup>R. V. Williams and P. W. Martin Electrodeposited Composite Coatings. British Iron and Steel Research Association, London, S W 11 (1964)

<sup>21</sup>U. S. Patent No. 3,132,927 Wear Resistant Material  
W. G. Borner 5/12/64

Another characteristic of colloids at their isoelectric point is their ability to form flocs and settle rapidly. Because the charge on the colloid is zero at the isoelectric point, mutual forces of repulsion are absent and collision of colloid particles with each other results in agglomeration.<sup>22</sup> In fact attempts have been made to quantitatively relate sedimentation rate and zeta potential.<sup>23</sup>

Experimental work was undertaken to investigate the alumina content of the cathode deposit as a function of the pH of the plating bath. Sedimentation tests were run concurrently to determine the effect of pH on sedimentation rate.

Description of Equipment and Materials Employed. The deposition cells employed in the pH studies were identical with the deposition tanks employed in the initial coulometer studies.

The sedimentation tests were made in graduated columns at the completion of each deposition test.

The bath employed for the deposition studies was the copper formate bath. Adjustment of the pH of the bath was made by additions of

<sup>22</sup>Riddick T. M. The Role of the Zeta Potential in Coagulation Involving Hydrous Oxides. First Water Conference, Technical Association of the Pulp and Paper Industry 6/4/63

<sup>23</sup>Dulin C. I. and Elton G.A.H. Determination of Electrokinetic charge and Potential by the Sedimentation Method. Part I Silica in Aqueous Solutions of Potassium Chloride J. Chem Soc. pp 286-9 1952

concentrated reagent grade sulfuric acid. The disperse phase in all tests was 25 grams per liter Linde-B-5125

Measurements of pH were made with a Beckman Zeromatic pH meter.

At the conclusion of each run the deposits were stripped from the cathode, copiously washed with water and analyzed for alumina.

The results of the experimental work are tabulated below:



## TABULATION OF RESULTS

Results of Deposition Studies Performed  
in Copper Formate Bath at Various pH's

Table - 7

pH of Electrolyte	Mls Conc H <sub>2</sub> SO <sub>4</sub> Reqd to obtain pH	Cell Voltage V.D.C.	Wt % Al <sub>2</sub> O <sub>3</sub> in deposit
4.0	0.0	2.30	1.95
3.5	2	2.22	1.74
3.0	4	2.32	2.09
2.5	15	2.82	1.63
2.0	19	2.10	1.57
1.5	33	2.00	1.45
1.0	64	1.11	2.03
0.5	106	0.83	1.74

The deposit content of the bath was also plotted as a function of pH. See Fig. (8)

From the sedimentation data the constant rate portion of the sedimentation curves was plotted. See Fig. (9)

The derivatives of the sedimentation curves were plotted as a function of the pH of the bath. See Fig. (10)

The alumina content of the deposit was then plotted as a function of the sedimentation rate of the bath. See Fig. (11)

Inspection of Fig. (8) indicates that no significant change in deposit content was experienced with decreasing pH.

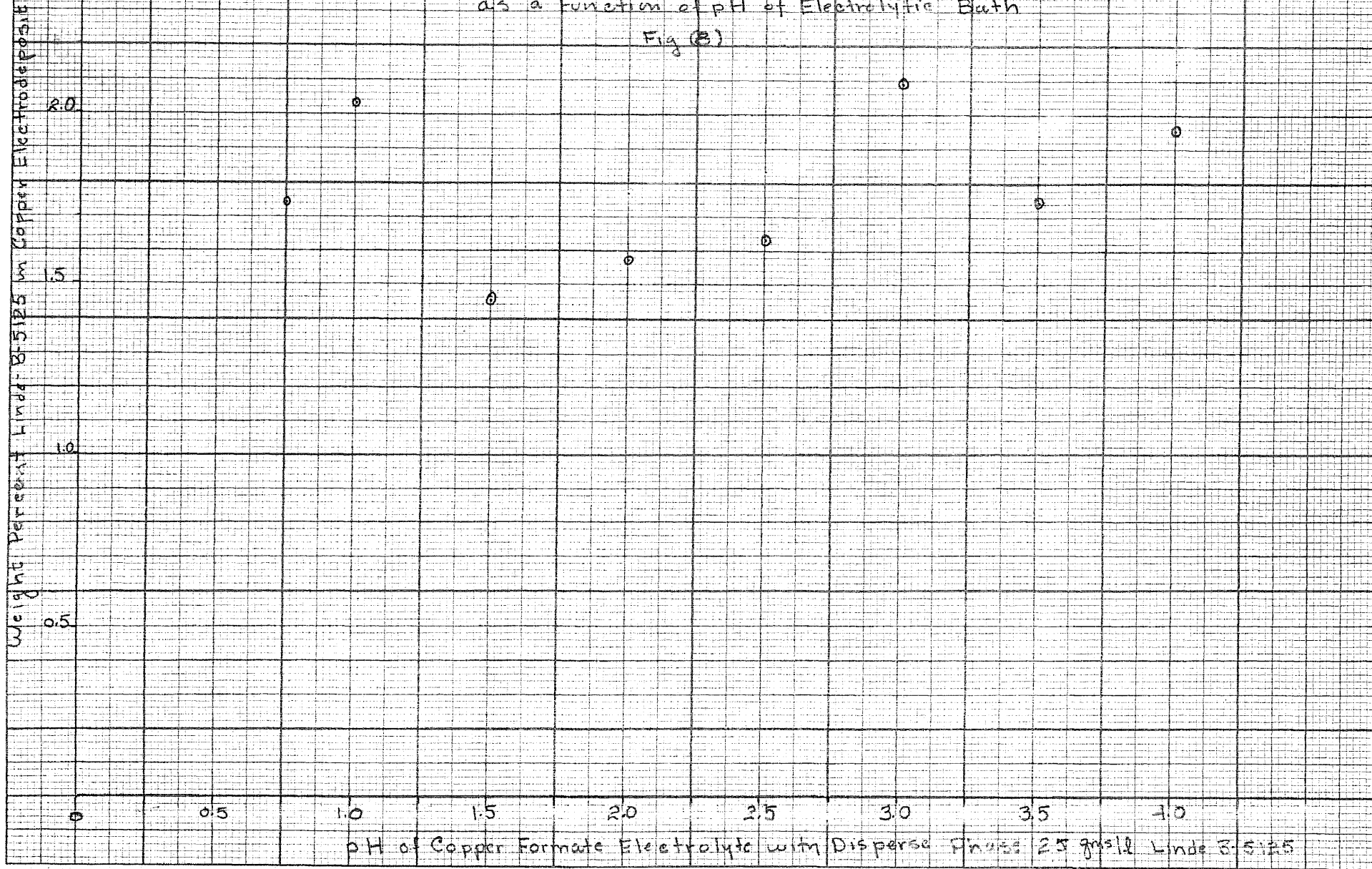
No abrupt increase in sedimentation rate was experienced, as would be anticipated if the alumina passed through an isoelectric point. See Fig. (10) In fact the sedimentation rate decreased with decreasing pH. The decrease can probably be attributed to the higher density of the electrolyte at lower pH's due to the large quantity of sulfuric acid required to depress the pH.

A plot of the deposit content as a function of sedimentation rate, see Fig. (11) showed no demonstrable relationship.

An observation worthy of note concerned the fact that the deposit obtained at pH - 0.5 contained a substantial amount of alumina, yet the copper sulfate, sulfuric acid bath which also operates at pH - 0.5 produced a deposit containing virtually no alumina.

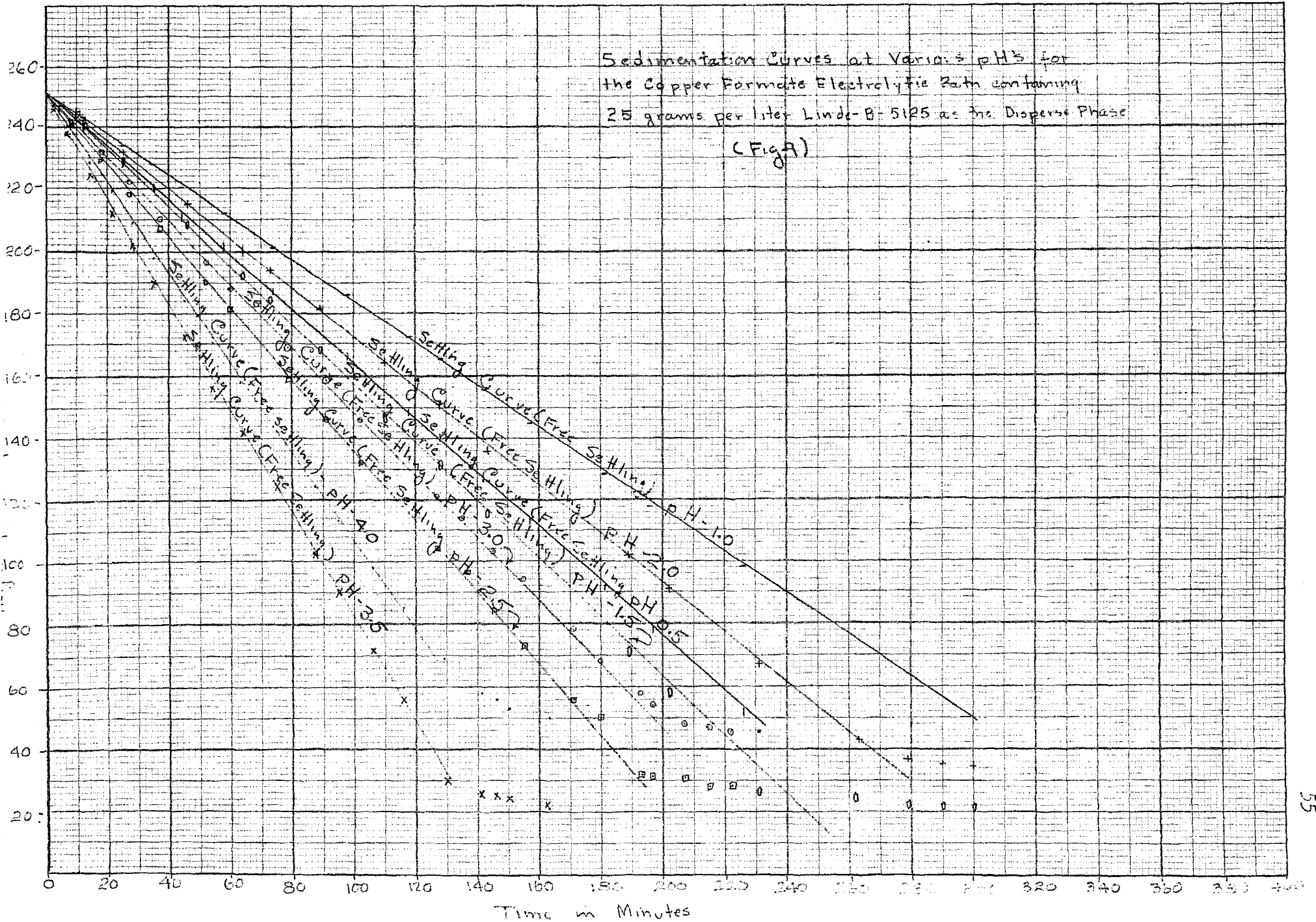
It may be concluded that the mechanism controlling co-deposition

Linde B-5125 Content of Electrodeposit  
 as a Function of pH of Electrolytic Bath  
 Fig (B)

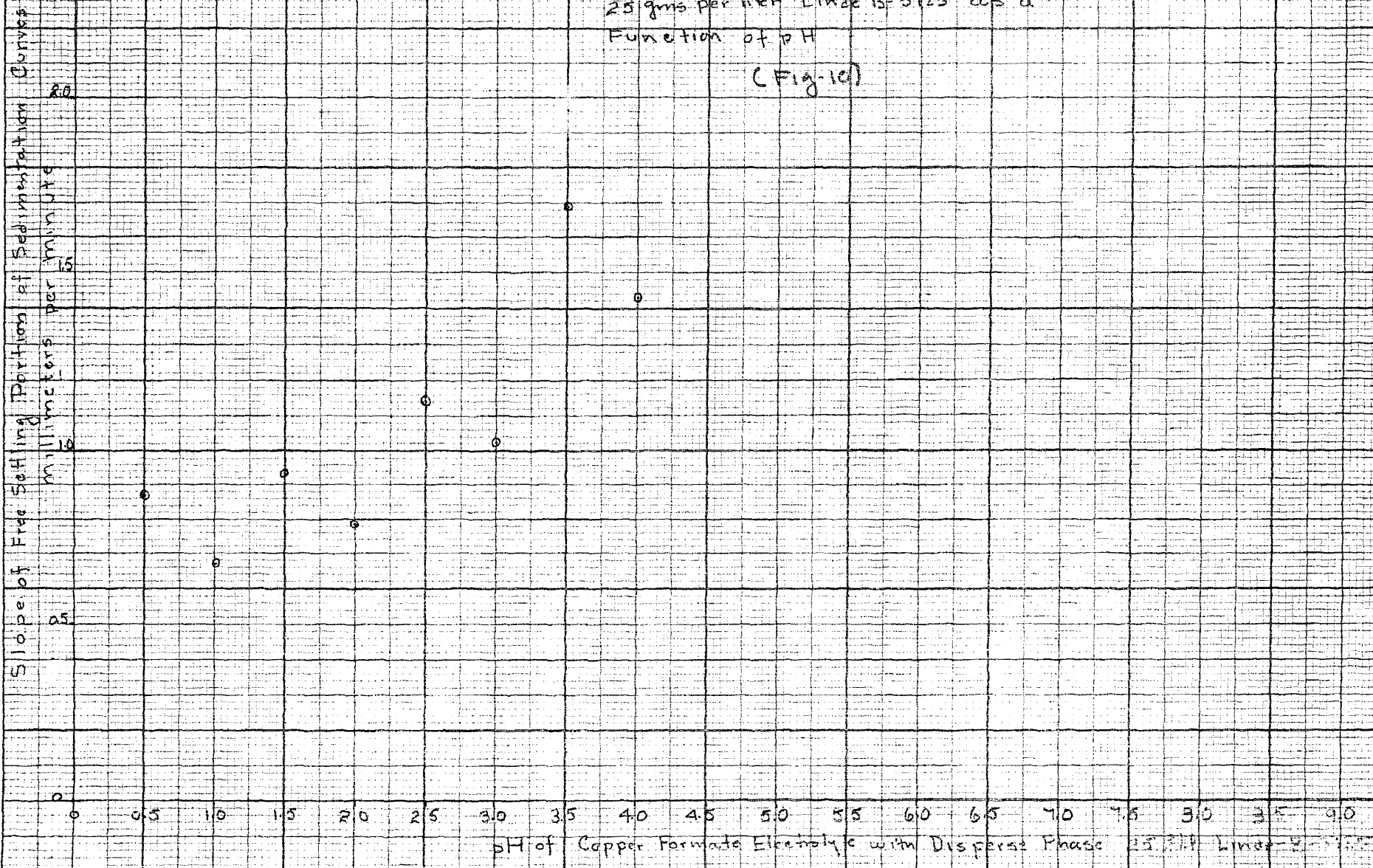


Sedimentation Curves at Various pH's for  
the Copper Formate Electrolytic Bath containing  
25 grams per liter Lind-B-5125 as the Disperse Phase

(Fig. A)



Free Settling Sedimentation Rate for  
 Copper Formate Electrolyte containing  
 25 gms per liter Linde B-5 P25 as a  
 Function of pH  
 (Fig. 10)



Linde B-5125 Content of Electrodeposit  
as a function of the slope of the Free  
Settling Portion of the Sedimentation Curves

(Fig. 11)

Weight Percent Linde B-5125 in Electrodeposit

20

15

10

0.5

0

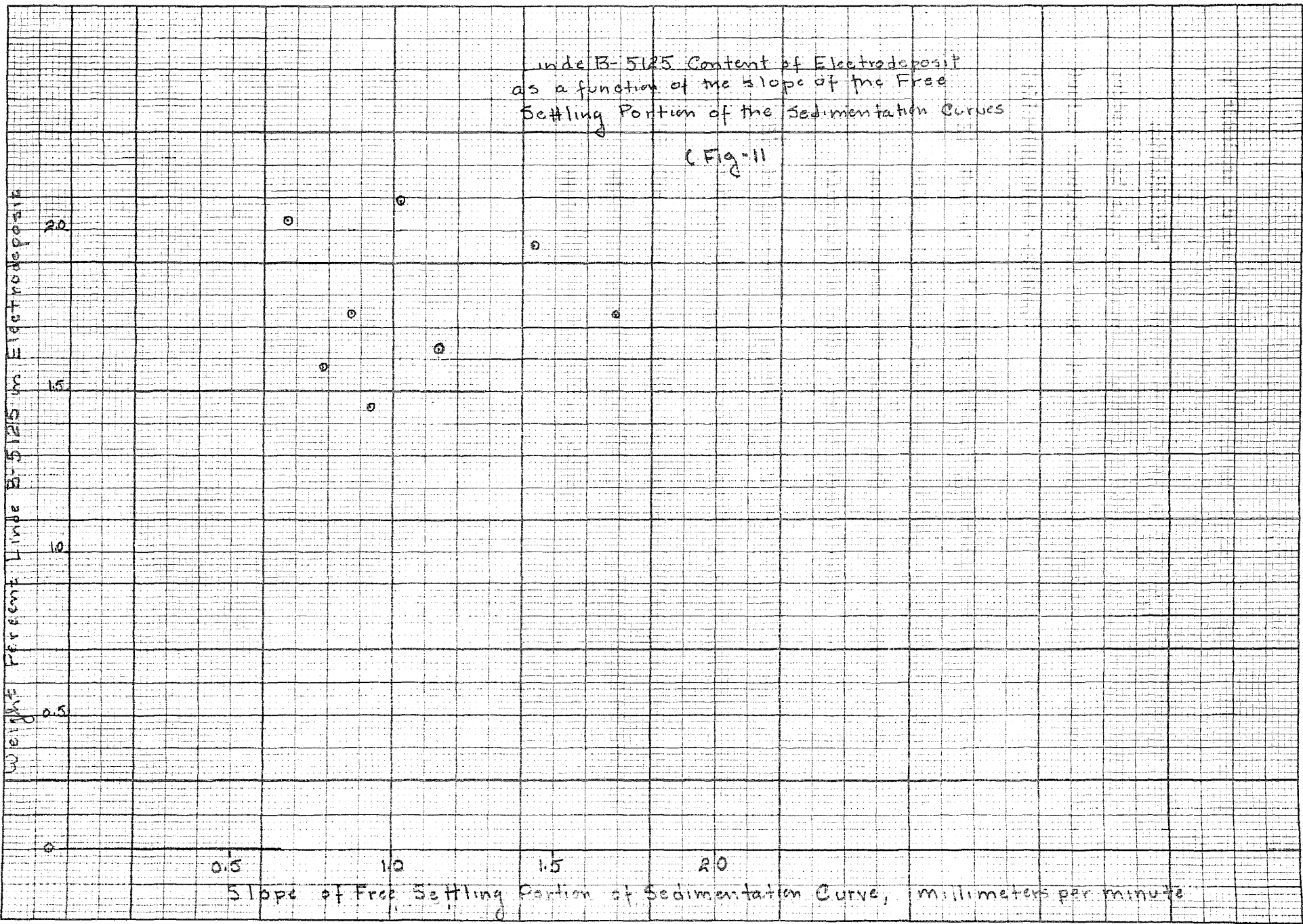
0.5

1.0

1.5

2.0

Slope of Free Settling Portion of Sedimentation Curve, millimeters per minute



of aluminas is not controlled solely by the pH of the electrolyte.

Conclusions. In conclusion it may be stated that no demonstrable evidence of electrophoretic control of the co-deposition of aluminas during electrolytic deposition of copper was established, based on the following observations.

- 1) Theoretical considerations suggest that the existence of a zeta potential is extremely unlikely in solutions of strong concentrated electrolytes such as those present in the electrolytic baths used in these studies.
- 2) No discernible migration of the alumina particles was detectable, other than in distilled water, in an electric field.
- 3) The pH of the electrolytes employed in the electrodeposition studies appeared to have no effect on the amount of alumina reporting in the cathode deposit.

## CHAPTER III

### CONSIDERATION OF ADSORPTION AS THE CONTROLLING MECHANISM FOR THE CO-DEPOSITION OF ALUMINA WITH COPPER DURING ELECTRODEPOSITION OF COPPER

#### Introduction:

The results of the experimental studies in Chapters I and II indicated that neither mechanical nor electrophoretic effects were the controlling factor in co-deposition of aluminas; however, both studies indicated that bath composition profoundly effects the amount of alumina co-deposited.

The hypothesis that a constituent in the electrolytic bath changes the nature of the surface of the alumina particle so as to allow it to be adsorbed on the copper cathode and be keyed into the copper matrix by copper electrodeposited over it would be consonant with the observations made in Chapters I and II.

#### Theory

The type of adsorption anticipated would be a short range Van der Waal's adsorption where the particles would have to be brought to within close proximity of the cathode in order for alumina particle to be held, by the weak electrostatic forces involved, long enough for copper to deposit on it and imbed it in the deposit.

In contradistinction to adsorption electrophoresis is controlled by long range forces, that is, the particles will migrate in an electric field, without mechanical assistance.



Previous studies of electrodeposition of copper from a copper sulfate, sulfuric acid bath containing thiourea and disperse phase of 25 grams per liter Alon-C<sup>1</sup> established that the presence of thiourea in the electrolyte, profoundly affected the amount of alumina co-deposited in the cathode.

The use of thiourea in copper sulfate, sulfuric acid baths as an additive to improve the quality of the electrodeposits is well known;<sup>24</sup> however, the mechanism by which thiourea modified the characteristics of the copper electrodeposit was only recently elucidated by Bacon, Hoekstra, Sison and Trivich.<sup>25</sup> The results of their investigation established that during the electrodeposition process thiourea was adsorbed on the cathode surface. Through the use of radioactive tracers it was established that thiourea was strongly and uniformly adsorbed.

If it could be proven that the aluminas employed in these studies adsorbed thiourea and further, that they then would co-deposit with copper during electrodeposition of copper in a copper sulfate, sulfuric acid bath substantiation of adsorption as the controlling mechanism for the co-deposition of aluminas with copper would be realized.

<sup>1</sup>Final Report to International Copper Research Assn. Electrodeposition of Dispersion Hardened Alloys, Opie, W. R. Ernst, R. G. Hoffmann, J. E. May 1, 1964

<sup>24</sup>Clifton, F. L. and Phillips, W. M. Proc. Am. Electroplaters Soc. 30 92 1942

<sup>25</sup>Bacon Ke, Hoekstra, J. J., Sison, B. C., Trivich, D. The Role of Thiourea in the Electrodeposition of Copper J. Electro Chem. Soc. V.106 May 1959

Accordingly, studies were undertaken:

- 1) To determine the quantity of thiourea adsorbed by aqueous dispersions of the various aluminas.<sup>26</sup>
- 2) To determine the effect of thiourea in the electrolytic bath on the amount of alumina co-deposited.

<sup>26</sup> Adsorption studies were made in aqueous solutions rather than actual electrolyte because the sulfate content of the electrolyte would make thiourea analysis impossible by conventional analytical techniques.

Experimental Procedure Part IAdsorption Studies.

Description of Materials Employed in Adsorption Studies. The four aluminas employed in the adsorption studies were described previously in Chapter - I. To obtain a qualitative idea of the adsorption capacities of the various aluminas their surface area was calculated.

Illustrative calculations are offered below for Alon-C. Since the method employed for calculating the area of Alon-C agreed well with actual surface area obtained by the B.E.T. method a similar technique was used to calculate the area of the other aluminas.

Average diameter of an Alon-C particle - 30 millimicrons

Volume of a sphere -  $4.189 r^3$

$$\begin{aligned} \text{Volume of a single Alon-C particle} &= (4.189)(15 \times 10^{-7})^3 \text{ cm}^3 \\ &= (4.189)(3.375 \times 10^{-18}) \end{aligned}$$

where the radius of the sphere is expressed in centimeters.

$$\begin{aligned} \text{Wt of a particle (Sp. Gr.} \times \text{vol)} &= (4.189)(3.42)(3.375 \times 10^{-18}) \\ &\qquad\qquad\qquad \text{grams} \\ &= 48.4 \times 10^{-18} \frac{\text{grams}}{\text{particle}} \end{aligned}$$

Surface area per gram of alumina (Alon-C)

$$\begin{aligned} &= \frac{1}{(48.4 \times 10^{-18}) (12.57) (15 \times 10^{-7})^2} \\ &= 58.4 \times 10^4 \text{ cm}^2 \\ &= 58.4 \text{ m}^2 \text{ per gram} \end{aligned}$$

Surface area per gram of Linde-B-5125 -  $14.2 \text{ m}^2$  per gram

Surface area per gram of Linde-A-5175 -  $5.84 \text{ m}^2$  per gram

Surface area per gram of 600 grit Alundum -  $0.103 \text{ m}^2$  per gram

The particles of alumina per gram are also given below:

Alon-C	-	$2.07 \times 10^{16}$
Linde-B-5125	-	$4.48 \times 10^{15}$
Linde-A-5175	-	$2.06 \times 10^{13}$
600 grit Alundum	-	$1.14 \times 10^8$

The thiourea used in the studies was Fishers Certified Reagent Grade Cat. No. T-101.

The purity of the thiourea was determined by the analytical procedure outlined below. The same procedure was employed in all subsequent thiourea analyses. Its reproducibility was confirmed by running blanks and duplicates, when possible, on the samples generated.

#### Procedure

The solution whose thiourea content was to be determined, was transferred to a 250 millimeter beaker and acidified by addition of a few drops of concentrated hydrochloric acid.

The solution was heated and bromine water was added to it until the red color of the bromine became permanent. The function of the bromine was oxidation of the sulfur in thiourea to sulfate ion. Nitric acid may also be used for the oxidation, but very careful control of the  $\text{HNO}_3$  concentration is required. Excess bromine was then expelled by boiling the solution.

Sufficient barium chloride was added to the solution to precipitate all sulfate ion present as barium sulfate.

The barium sulfate was digested for a minimum of an hour, then filtered onto Whatman-42 ashless paper. The filter paper with the barium sulfate was transferred to a tared porcelain crucible and fired to a constant weight.

Thiourea content was calculated as

$$\text{Weight of residue after firing} \times \frac{76.10}{233.40} = \text{Weight Thiourea}$$

Adsorption Studies Experiments Performed. In order to determine the quantity of Thiourea adsorbed on the various aluminas, samples containing 25 grams per liter of the four aluminas and 1 gram per liter thiourea in an aqueous solution were prepared.

The aqueous alumina suspensions were stored in sealed containers and periodically shaken. After standing, with periodic shaking, for four days the suspensions were centrifuged in an International Centrifuge, Size-1 Type C, for several hours. Examination of the samples after centrifugation revealed that in no case had a clear supernatant liquid been obtained.

New samples were prepared and gravity filtration studies undertaken. The results of these tests showed that 600 grit Alundum, Linde-A-5175 and Linde-B-5125 could be filtered off by repeatedly passing the filtrate back through the filter paper.

In order to separate the Alon-C from the suspension by gravity filtration, it was necessary to first precoat the filter paper with Linde-B-5125. The Alon-C suspension was filtered through the pre-coated paper and the filtrate discarded until the filtrate from the Linde-B suspension had been flushed out of the filter paper.

During all filtration studies the equipment containing alumina suspensions was covered to avoid loss of water by evaporation. The results of the adsorption studies are tabulated below:

#### TABULATION OF RESULTS

##### Results of Adsorption Studies

Concentration of Thiourea in Solution - 1.0 grams per liter

Concentration of Alumina in Suspension - 25 grams per liter

Table - 8

Suspended Phase	Surface Area of Alumina - m <sup>2</sup> gm	Grams of Thiourea Adsorbed Grams of Alumina Present
Alon-C	58.4	Less than 0.001
Linde-B- 5125	14.2	Less than 0.001
Linde-A 5175	5.8	Less than 0.001
600g Alundum	0.10	Less than 0.001

From the preceding tabulation it may be concluded that the amount of thiourea adsorbed, if any, was so exceedingly small as to be outside the precision of the analytical technique employed.

Experimental Procedure Part IIElectrodeposition Studies.

Description of Equipment and Materials. The electrolytic cells for studying the effect of thiourea on the amount of alumina co-deposited during electrodeposition of copper in a copper sulfate, sulfuric acid bath are described below:

Plating tanks - 6.0" wide by 3-1/4" deep by 9-3/4" high

Cathodes - Stainless Steel - 7" by 2-3/8"

Anodes - OFHC (reg. trade) copper - 7" by 2-3/8"

The anode and cathode were placed at opposite ends of the tank in vertical parallel planes 5-1/2 inches apart.

The plating conditions and bath composition for each run are offered below. The current density employed in all tests was 30 amperes per square foot and the temperature of the plating bath was 25°C.

## Bath Composition

CuSO <sub>4</sub> 5H <sub>2</sub> O	-	188 grams per liter
H <sub>2</sub> SO <sub>4</sub>	-	74 grams per liter
Molasses	-	2 grams per liter
Thiourea	-	100 milligrams per liter

## Disperse Phase

Run - 1	25 grams per liter	Alon-C
Run - 2	25 grams per liter	Linde-B-5125
Run - 3	25 grams per liter	Linde-A-5175

Run - 4            25 grams per liter    600 grit Alundum

At the conclusion of each run, the deposits were stripped from the cathode and analyzed for alumina by the method described in Chapter-I.

The results of the tests are tabulated below. Offered for comparison are the alumina contents of deposits obtained on the bottom cathode surfaces for the copper sulfate, sulfuric acid bath studied in Chapter-I of this paper. The composition of the sulfuric acid, copper sulfate bath used in Chapter-I is identical with the bath composition employed in this study, with the exception of thiourea.

Also included in the tabulation is the ratio of the molecules of thiourea to the number of alumina particles in the bath.



## TABULATION OF RESULTS

Alumina Content of Deposits Obtained in the Copper

Sulfate Electrolyte With and Without Thiourea

Table - 9

Disperse Phase Conc. 25g/l	Molecules of Thiourea Per Alumina Particle	Wt % Alumina in Cathode Deposit Thiourea in elec- trolyte-100 <sup>mg</sup> /l	Wt % Alumina in Cathode Deposit-No Thiourea in Electrolyte
Alon-C	$1.47 \times 10^3$	0.60	0.026
Linde-B- 5125	$7.07 \times 10^3$	0.73	0.042
Linde-A- 5175	$1.53 \times 10^6$	0.65	0.029
600 grit Alundum	$2.78 \times 10^{11}$	0.92	0.021

SUMMARY OF CONCLUSIONS CHAPTERS I II AND III

The results of the experimental work performed along with theoretical considerations allow the following conclusions to be made.

Mechanical inclusion does not appear to control the co-deposition of aluminas with copper. This conclusion was definitively established by plating studies in copper plating baths of different composition; where it was shown that varying the composition of the bath increased the alumina content of the electrodeposits by factor of approximately sixty.

The pH of the copper electroplating bath appears to have no significant effect on the amount of alumina co-deposited with copper. The copper formate bath at a pH of 0.5 produced a deposit containing a substantial amount of alumina while the copper sulfate, sulfuric acid bath at the same pH produced deposits containing virtually none. Further evidence of alumina co-deposition being independent of the pH of the plating bath was obtained when it was shown that the addition of small amounts of thiourea to a plating bath caused a large increase in the amount of alumina in the electrodeposit.

No evidence of electrophoretic affects controlling co-deposition of aluminas was obtained. Experimental measurements of the zeta potential of the aluminas did not indicate that a zeta potential existed in the systems studied. The results of the experiments were in agreement with the predictions based on theory.

The possibility of adsorption controlling the co-deposition of aluminas may not be precluded on the basis of the experimental work performed. The results of studies performed neither substantiate or disprove the theory of adsorption.

## RECOMMENDATIONS

The results of the studies performed confirm the findings of previous investigations; that it is possible to produce dispersion hardened alloys of copper with a disperse phase of alumina by electro-deposition.

The alloys of copper and alumina produced by electrodeposition, were highly unsatisfactory with regards to their physical properties.

The alloys were extremely brittle, and very weak mechanically. Attempts to stress relieve the alloys by annealing caused them to crack and curl.

It is recommended that means other than electrodeposition be sought for production of dispersion hardened copper alumina alloys.

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