ELECTRODEPOSITION OF CELLULOSE
AND CARBOXYMETHYLCELLULOSE

BY

CHARLES E. DRIESENS, JR.

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ABSTRACT

The previous work done by Frank Cozzarelli on the electrodeposition of cellulose from a sodium zincate-urea-cellulose system has been verified, except that zinc was found to deposit on the cathode at all voltages and current densities within the range of the optimum conditions for deposition. The optimum conditions are: voltage - 1.10 to 1.28 volts; current density - 0.13 to 1.10 amperes/square foot; electrode material - copper. Current efficiencies range from 0.80 to 5.53%.

A chelate-like complex formed from the sodium zincate and urea which couples with the cellulose has been proposed as a possible explaination of the mechanism governing the electrodeposition of cellulose; the proposal is based on analytical data obtained on deposits.

The optimum conditions for the electrodeposition of both medium viscosity and high viscosity grades of carboxymethylcellulose have been determined and are: voltage - 2.50 to 3.00 volts; current - 42 to 66 milliamperes; current density - 0.47 to 0.75 amperes/square foot; electrode material - copper or nickel. Current efficiencies found were: for medium viscosity - 0.186 to 0.213%; for high viscosity - 0.084 to 0.098%.

The electrochemical equations governing the deposition have been determined from analytical data obtained during the study. The mathematical relationship for current and voltage, and for current and weight of deposition for both grades of carboxymethylcellulose have been derived; the average deviation obtained in using the relationships for computations is 8%.

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ELECTRODEPOSITION OF CELLULOSE
AND CARBOXYMETHYLCELLULOSE

INTRODUCTION

The experimental work on the electrodeposition of cellulose was originally undertaken by Cozzarelli (2)(11). The work, reported herein, is a continuation.

Cozzarelli's initial work consisted of the investigation of the possibility of depositing, electrolytically, regenerated cellulose from a solution of cellulose in aqueous sodium zincate-urea. The work explored electrodeposition from solutions containing from 0.5% to 2.5% of dissolved cellulose using various types of metallic electrodes. Determination of the optimum conditions of voltage, current, current density, and concentration of cellulose for the electrodeposition on the best suited electrode material was made. Cozzarelli further suggested the possibility of introducing "additives" to the sodium zincate-urea-cellulose system to improve the nature and characteristics of the electro-deposited cellulose films.

The present study was concerned with two phases:

First - A continuation of the study of the sodium zincate-urea-cellulose system in an endeavor to improve the deposition of cellulose. Largely, analytical means were employed to determine the nature of the films produced.

Second - A study of the electrodeposition of carboxymethylcellulose, the types of films produced, and the possible use of carboxymethylcellulose as an additive for the sodium zincate-urea-cellulose system.

Experimental Details

All experimental work was conducted using a 6 x 6 x 10 inches battery jar filled with 750 milliliters of the plating solution. Three different plating solutions were used during the course of the experiments:

(1) Sodium zincate-urea-cellulose which contained 1% by weight of dissolved cellulose. This was the solution used by Cozzarelli in his previous work.

(2) 1% aqueous solutions of

 (a) Medium viscosity grade carboxymethylcellulose gum,

 (b) High viscosity grade carboxymethylcellulose gum.

(3) A blend consisting of 75% by volume of sodium zincate-urea-cellulose and 25% of 1% medium viscosity carboxymethylcellulose.

The electrical current necessary for the experiments was obtained from a rectifier supplied by a 110 volt, 15 ampere laboratory supply line. The rectifier converted the alternating current supply to direct current. A Weston volt-ammeter was used to measure voltages, and a Triplett volt-ohm-mil-ammeter was used to measure currents and resistances. Conductivity of the plating solutions was measured with a Surfass conductivity bridge using a clear platinum electrode. Details of the rectifier and instruments are given in Appendix A.

Electrodes for the plating runs consisted of copper, nickel, and zinc, 2 x 8 inches (18 to 20 gauge sheet stock), immersed to a depth of 3.0 to 3.2 inches in the plating solution, and set either 1 centimeter or 1 inch apart between the plating faces of the electrodes for different runs. The electrodes were hung on copper rods (1/2 inch diameter) to which the direct current was supplied. All electrodes, before use, were dipped in 20% by volume of nitric acid, rinsed with water, dried, and then weighed on an analytical balance to the nearest milligram. The weight of cellulose or carboxymethylcellulose deposited was determined by the gain in weight of the anode.

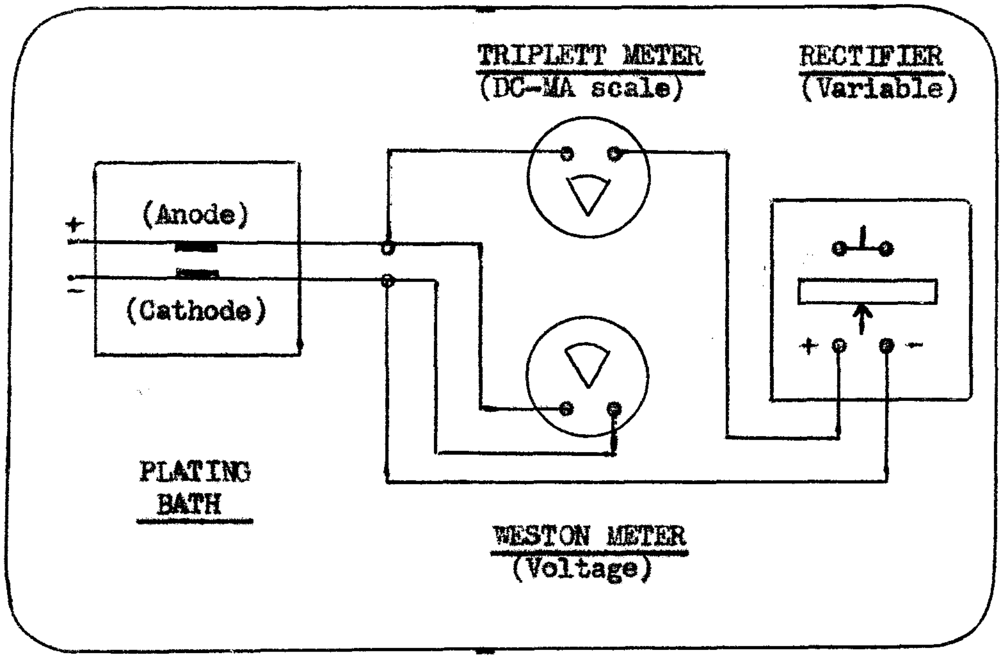
Electrolytic deposits of cellulose were first rinsed free of adhering solution with water, and then treated by various means employing both different acids and different concentrations of the various acids. Acid treatment was followed by dipping in water to remove residual acid, dipping in methanol to speed drying, air drying, and weighing (cellulose still on anode). The dried deposit was removed from anode by peeling or scraping.

Carboxymethylcellulose deposits were rinsed free of adhering solution with water, dipped in methanol, air dried, and weighed. Once weighed, the deposits were removed from the anodes by peeling or scraping.

In most of the plating runs made, only measurements of the weight of the electrodes before and after the run and of current and voltage were taken. In a few runs additional measurements were made of resistance of the plating system and of conductivities of the plating solutions. Ash contents at 800° C. were determined on a majority of the deposits produced - a few deposits were subjected to more thorough analyses.

Circuit

The electrical circuit used for the experiments was as follows:



Efficiency of Electrodeposition

One equivalent weight of a compound is deposited by 96500 coulombs in accordance with Faraday's laws of electrodeposition (9). Coulombs are ampere-seconds. Thus, the relationship:

$$\frac{\text{Amperes x (Time interval in seconds)}}{96500}$$

will give the fractional part of one equivalent weight that can theoretically be plated during the given time interval. One equivalent weight of a compound is found by dividing the molecular weight by the valence. Therefore, the theoretical weight of deposition for a given time interval will be:

$$\text{Theoretical weight deposited (Expressed in grams)} = \frac{\text{Amperes} \times \text{seconds} \times \text{molecular weight}}{96500 \times \text{valence}}$$

The percentage of current efficiency of deposition is given by:

$$\text{Efficiency} = \frac{\text{Weight of deposit}}{\text{Theoretical weight deposited}} \times 100$$

Or:

$$\text{(A)} \quad \text{Efficiency} = \frac{\text{Weight of deposit} \times 96500 \times \text{valence} \times 100}{\text{Amperes} \times \text{seconds} \times \text{molecular weight}}$$

The molecular weights and valences of the compounds used in this study are given as: (from references (2), (3), and (5))

		Molecular weight	Valence
Cellulose	(average)	50,000	2
Medium viscosity carboxymethylcellulose	(average)	150,000	1
High viscosity carboxymethylcellulose	(average)	300,000	1

For a plating run of 15 minutes duration for the cellulose and carboxymethylcellulose used, expression (A) reduces to:

$$\text{(B)} \quad \text{Efficiency of cellulose electrodeposition} = \frac{\text{Weight of deposit}}{\text{Amperes}} \times 0.429$$

$$\text{(C)} \quad \text{Efficiency of med vis carboxymethylcellulose electrodeposition} = \frac{\text{Weight of deposit}}{\text{Amperes}} \times 0.0715$$

$$\text{(D)} \quad \text{Efficiency of high vis carboxymethylcellulose electrodeposition} = \frac{\text{Weight of deposit}}{\text{Amperes}} \times 0.0357$$

where weight of deposit is in grams.

PART I -

ELECTRODEPOSITION OF CELLULOSE

PREVIOUS WORK

Cozzarelli (2) has shown that cellulose can be plated from a sodium zincate-urea solution using copper electrodes. Optimum conditions were found to be:

Voltage	1.10 - 1.28 volts
Current density	0.137 - 1.11 amperes/square foot
Efficiency	1.0 - 3.3 %

The optimum conditions were achieved using a plating solution composed of:

Cellulose	1.0 %	(by weight)
Sodium Hydroxide	10.0 %	" "
Zinc oxide	4.5 %	" "
Urea	10.0 %	" "
Water	74.5 %	" "

At a potential greater than 1.28 volts, Cozzarelli found that zinc deposited on the cathode.

Cozzarelli showed that the film deposits were cellulose by the following methods:

(1) The deposit was scraped from the anode after drying, dissolved in sulfuric acid and refluxed to cause hydrolysis to glucose;

(2) Glucose was determined by use of Fehling's solution;

(3) The deposit was shown to be insoluble in hot water and soluble in Schweitzer's reagent which is a test for cellulose.

CONTINUATION OF ANALYSIS

In an effort to learn more about the nature of the films produced, additional analytical methods were employed in the present study. Two separate plating runs were made, the anodic deposits were permitted to air dry without use of acid treatment in order to preserve all deposit constituents. When dry, the deposits were scraped from the anodes and combined to provide sufficient for many analyses. The combined deposits were analyzed using the following methods:

(1) Ash content (weight percent) was determined at 800° C.

(2) Analysis of the ash for copper and zinc. Copper was determined by electrodeposition from a dilute sulfuric acid solution of the ash, and zinc from the same solution by versene titration using eriochrome black T as indicator.

(3) Ash acid insolubles (weight percent) was determined by filtration of the insolubles from the sulfuric acid solution of the ash prior to determination of the copper and zinc.

(4) Sodium in the deposit was determined with a flame photometer.

(5) Nitrogen in the deposit was determined by the Kjeldahl method.

(6) Carbon, hydrogen, and oxygen analysis were made by standard combustion tube methods.

(7) Basic nitrogen in the deposit (to show the nature of urea in the deposit) was determined by electrometric titration with standard (0.05 N) perchloric acid in glacial acetic acid solution.

(8) Biuret reaction test was made with dilute copper sulfate solution. This test was made to determine whether the urea was combined in a protein-like bond or not.

Results on the combined deposits of Runs 14 and 15 were:

	CONSTITUENT WEIGHT PERCENT IN	
ANALYSIS FOR	DEPOSIT	ASH
Ash at 800° C.	(46.85)	
Insolubles (SiO_2, R_2O_3)	2.13	4.47
Copper	2.17	4.55
Sodium	16.59	34.85
Zinc	15.71	33.00
(Oxygen in ash - calculated on basis of the oxides, Na_2O, CuO, ZnO)	(10.17)	21.36
(Total constituents of ash)		98.33 %
Carbon	17.62	
Hydrogen	3.70	
Oxygen - by analysis	20.65	
Nitrogen	11.59	
(Total constituents of deposit, excluding calculated oxygen)	90.16 %	
(Total constituents of deposit, including calculated oxygen)	100.33 %	
Basic nitrogen	Nil	
Biuret reaction	Nil	

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The molecular formulas and percentages of the constituent elements for urea and cellulose are:

	Urea (NH_2CONH_2)		Cellulose $(C_6H_{10}O_5)_x$
Molecular weight	60.06	Molecular weight	162.14
Carbon	20.00 %	Carbon	44.44 %
Hydrogen	6.71	Hydrogen	6.22
Oxygen	26.64	Oxygen	49.34
Nitrogen	46.65		
	100.00 %		100.00 %

On the basis of the nitrogen analysis for the deposit and assuming that the nitrogen is deposited as urea, the percent by weight of urea in the deposit would be:

$$11.59 \times \frac{60.06}{28.02} = 24.84\ \%$$

In strongly alkaline solution, urea will slowly decompose according to the reaction (8), yielding ammonia and sodium bicarbonate in the case of the sodium zincate-urea system:

$$NH_2CONH_2 + H_2O \longrightarrow 2\ NH_3\uparrow + CO_2$$

$$CO_2 + NaOH \longrightarrow NaHCO_3$$

These reactions and the absence of basic nitrogen would indicate the absence of ammonia in the deposit.

The percentage of ash plus the calculated percentage of urea would give the deposit the following composition:

Ash	46.85 %
Urea	24.84
Cellulose	28.31
	100.00 %

By calculating the percentages of each element from the molecular formulas and the foregoing results, the following data is obtained:

		PERCENTAGES OF			
		CARBON	HYDROGEN	OXYGEN	NITROGEN
Ash	46.85	—	—	—	—
Urea	24.84	4.97	1.67	6.62	(11.59)
Cellulose	28.31	12.58	1.76	13.97	—
Total %	100.00	17.55	3.43	20.59	(11.59)
By analysis		17.62	3.70	20.65	11.59

Several points must be considered in evaluating the above.

(1) The analyses are accurate within 0.20%, since sample sizes used for analysis were of 10 to 20 milligrams (semi-micro balance) the second decimal place is doubtful.

(2) The oxides of the metals, Na_2O, CuO, and ZnO are all stable above 1120° C. at which temperature the analysis for oxygen is made. Therefore oxygen present in the form of an oxide or in a salt such as sulfate is not determinable by the method employed.

(3) The value for hydrogen can be high or low depending upon the extent that NaOH or $NaHCO_3$ is present or absent in the deposit.

(4) The missing 1.7% from the total of the analyses for the components of the ash could be in the form of the chloride, sulfate, or metals not analysed for.

(5) The results for the ultimate analyses will not necessarily be the same for each and every deposit produced electrolytically. This is shown by the difference between the ash content of the combined deposits of Runs 14 and 15 and the ash content of Run 25 (see Table 2, appendix).

SODIUM ZINCATE-UREA SOLVENT

The sodium zincate-urea solvent is stable only for short periods of time. When standing for more than a week, the odor of ammonia can be detected when the container is opened. On longer standing, the odor of ammonia grows progressively stronger as the solution ages. The urea breaks down in accordance with the reaction previously given (p. 9).

One lot of sodium zincate-urea-cellulose standing from June until September - 3 months - failed to produce cellulose deposits (Runs 20 and 21), yet in June had produced satisfactory deposits (Runs 17 and 19). The maximum time for satisfactory deposition from a batch of solvent is placed at 6 to 8 weeks.

It has been found experimentally that making the solvent in the following manner produces more effective solution of the cellulose:

(1) The zinc oxide is weighed into a 1 liter Erlenmeyer flask (203 grams or 7 ounces); 300 ml of water are added and well shaken to produce a paste.

(2) About 1/3 of a pound of sodium hydroxide (either in pellets or flakes) is added directly. The flask is vigorously agitated with a swirling motion while being held in a stream of cold water to take up the heat produced. When the first 1/3 is in solution and with the solution still hot, the second 1/3 pound of sodium hydroxide is added and the procedure repeated. The final 1/3 pound is then added, again with vigorous swirling. As solution progresses, the paste becomes thinner.

(3) When the flask starts to cool, an additional 200 ml of water are added and well mixed. A little ZnO and NaOH may remain undissolved - the solution at this point (when cool) may be transferred to a storage container having a 1 gallon capacity. The undissolved ZnO and NaOH remaining in the flask are put into solution by adding 100 ml of water and placing on a hot plate (or steam bath) for a few minutes until solution is completed, this in turn is added to the storage container, with an additional liter of water.

(4) A pound of urea is separately dissolved in a liter of water, and when completely in solution, is added to the storage container. An additional 800 ml are added, to bring the total volume of water to 3400 ml. The solution should be well mixed with each addition. The total volume at this point will be about 1 gallon.

(5) 45 grams (1.6 ounces) of cellulose are added. It may take from about an hour to a day to dissolve the cellulose depending on the type used. Rayon (regenerated cellulose) will go into solution in about an hour, filter paper will take a day.

In the preparation of one batch, the undissolved zinc oxide was filtered out and weighed. Zinc oxide constitutes 4.5% by weight of the total weight of the sodium zincate-urea solvent, and it was found that 87% dissolved in the sodium hydroxide, 13% (equivalent to 0.6% of the total solvent) remained insoluble.

REMOVAL OF ANODIC DEPOSITS BY ACID TREATMENT

Cozzarelli (2) indicated the necessity for acid treatment of the cellulose deposits produced in order to facilitate the removal of the deposit from the anode. Cozzarelli used 50% (6 normal) hydrochloric acid to treat the deposits. 50% HCl produces a vigorous reaction with the deposit resulting in the evolution of gases (CO_2, H_2) which in turn tend to cause mechanical breakup of the cellulose film - the gas bubbles disengage particles from the film. In order to circumvent the destruction of the film during acid treatment, more dilute solutions of hydrchloric, acetic, and nitric acids were employed in the present study. The effect of the various acid treatments on the ash content of the treated deposits is summarized in Table 2 (appendix).

The data obtained indicate that the more dilute the acid, the more cellulose remaining in a compact film at the end of the acid treatment, and that more time is necessary to effect dissolution of the alkali in the deposit. Treatment with 20% acetic acid for 10 to 15 minutes produces films with ash contents of about 9.0%; treatment with 20% HCl for 5 minutes yields films with ashes in the range of 21 to 35% while 10 minutes of treatment with 20% HCl gives ashes in the order of 1 to 4%. 20% nitric acid produces similar results to 20% HCl - 5 minutes yields films with high ashes, 10 minutes produces cellulose having ashes under 4%.

Even with the various methods of acid treatment tried, difficulty is still experienced in removing the cellulose from the electrodes. Cellulose deposits are fragile, very friable, and delicate. It is felt that much more exploratory work is needed in this phase of the electrodeposition of cellulose before a commercial process and uses are sought.

EFFICIENCY OF DEPOSITION

The current efficiencies obtained for the various plating runs made are tabulated as part of the general data in Table 1 (appendix). These, in general for acid treated cellulose films, are of the same order of magnitude as those found by Cozzarelli.

Because efficiency calculations are based on the weight of cellulose after acid treatment, and as the influence of the mode of acid treatment shown by the ash analysis varies (from 1 to 60% ash), efficiencies are to the end of the present work very nebulous. Efficiencies are not, in the electrodeposition of cellulose, an abstract measurement contrary to previous thoughts. A higher ash content in the residual cellulose after acid treatment yields what appears to be a nice efficiency - in actuality residual alkali is being weighed along with the cellulose. More satisfactory acid treatment producing a lower ash, hence purer residual cellulose, shows poor efficiency. Current efficiencies, calculated as cellulose using the total weight of the deposits - alkali, urea, plus cellulose - before acid treatment, vary from 24 to 67% (see Table 1 for Runs 30 to 35, 48, 51); while for the same runs, on the basis of the acid treated cellulose, the efficiencies vary from 0.7 to 5.5%. For Run 31, the efficiency was also calculated from the zinc deposited on the cathode and is 28.3% compared to 0.87% based on the acid treated cellulose for the same run.

By both HCl and HNO_3 treatment for 10 minutes using 20% acid solutions, cellulose films containing under 4% ash appear to be produced regularly. This then would serve as a criterion upon which to calculate efficiency - in other words the acid treatment should be specified, the ash content given, then the efficiency expressed.

Actual efficiency is greater than that based on treated cellulose alone, because the deposit, as shown by the earlier presented analytical data, contains deposited alkali and urea as well as cellulose. The alkali and urea require current, unavoidably as part of the system's complex, for their co-deposition with cellulose.

Care is a keynote in the acid treatment of the deposits. Use of more dilute acids for the treatment means less mechanical loss of the cellulose during treatment, and hence greater efficiency.

As a consequence of the mathematical expression - equation (A) and its reduced form (B), page 5 - used to calculate current efficiency, there is a direct relationship between weight of deposition and efficiency, and an inverse relationship between current and efficiency. Current density, since it is directly proportional to current (in these experiments, the electrodes were immersed to 3.2 inches for all plating runs for a total plating surface of 0.089 square feet), also has an inverse relationship to efficiency. Higher current densities, however, cause less deposition of total solids which was observed by Cozzarelli as well, but between current density and less deposition there appears to be no mathematical relation.

Runs having the best current efficiencies were made under an applied potential of 1.25 to 1.30 volts. Because of the variances obtained in efficiency for these runs (2.0 to 5.5%), no correlation between voltage and efficiency is apparent.

MECHANISMS IN THE ELECTRODEPOSITION OF CELLULOSE

Urea has been termed a lyophilic compound by Heuser (5), and Weiser (15) describes the mechanism by which lyophilic compounds in alkaline and acid media assist in the hydration of colloids.

Zinc in alkaline media will form chelate complexes (12) of the type:

$$\left[Zn(NH_3)_2\right]^{2+} \text{ and } \left[Zn(NH_2CH_2CH_2NH_2)\right]^{2+}$$

The lack of basic nitrogen in the deposit, although nitrogen is present, would indicate that the urea is in some form of a complex either with the sodium and zinc, or with the cellulose, or both. Mantell (10) has demonstrated the ability of urea to aid in the dissolution of cellulose in sodium zincate and sodium stannate systems.

The ability of urea to form trimers with aldehyde groups (8) is the basis of many commercial processes for the production of resins. Cellulose has the ability to form triesters and it possesses free aldehyde groups.

The possibility therefore exists of the formation of a chelate-like complex between the sodium zincate and the urea of the type:

$$Na_2\left[Zn(NH_2CONH_2)\ (OH)_4\right]$$

which in turn would couple with the aldehyde groups in cellulose aiding in the dispersion of the cellulose in the aqueous media.

Martell and Calvin (12) point out that specific conductance increases many fold when chelate complexes are formed in solution. The high conductivity measurements made for the sodium zincate-urea and the sodium zincate-urea-cellulose solutions (see Table 9, appendix) compared to water and solutions of carboxymethylcellulose seem to substantiate the formation of a chelate complex while the higher conductivity of sodium hydroxide makes the formation of a chelate complex doubtful. A 10% solution of sodium hydroxide, since conductivity is a function of concentration (9), will have a high value.

The reaction to form sodium zincate from sodium hydroxide and zinc oxide may be expressed thusly:

$$2\ NaOH + ZnO \longrightarrow Na_2ZnO_2 + H_2O$$

From the amounts of NaOH and ZnO used in these experiments to prepare Na_2ZnO_2, about 11 moles of NaOH and 2.5 moles of ZnO were added to each batch of solvent. 5 moles (approximately) of NaOH would react with the ZnO to form Na_2ZnO_2, leaving in excess 6 moles of NaOH. The excess NaOH would by its high conductivity cloud the true conductivity measurements of any complex formed. Whether or not such a complex is or is not formed can be determined by separation of sodium zincate and measurement of its conductivity alone, in urea solution, and in urea solution with cellulose.

As a chelate-like complex would aid in the dissolution of cellulose, electrodeposition would be causative in either breaking down the complex or depositing it in its entirety. From the analysis of the combined deposits of Runs 14 and 15, approximately 2 moles of sodium, 1 of zinc, and 1 of urea(which correspond to the suggested formula for the complex) were deposited for every 1/4 of a molecular unit of cellulose, but this does not hold for each and every run. On the basis of the differences in weights between the acid treated cellulose residue and the total deposit for Runs 33, 34, 35, and 48 less than 10% of cellulose was deposited in these runs. A similar comparison for other runs shows the percentage of cellulose to be even smaller. The mechanical loss of particles of cellulose has been cited and could cause smaller percentages in some runs, but mechanical loss alone is insufficient to explain these differences. Incomplete formation of sodium zincate in the preparation of the solvent, contamination from impurities in the components, and degradation of the solvent with age by loss of ammonia may all contribute - yet the differences (as indicated by efficiencies) follow no conclusive pattern or trend.

Deposition may be an intermediate between true deposition of cellulose (as proposed by Cozzarelli) and the deposition of a complex. How much sodium zincate-urea would be entrapped by either mode of deposition is unknown. Because of the wide range of results found, uncertainty as to the actual electrochemical equations involved in the deposition of cellulose remains.

SUMMARY OF DATA

Cozzarelli's results have been verified, except that in the present experiments zinc was found to deposit on the copper cathode at all voltages and current densities within the range of optimum deposition for cellulose.

When the applied potential has exceeded 1.30 volts with a current density exceeding 1.20 amperes/square foot, cellulose deposits, if produced, slough off and do not adhere to the anode. If the applied voltage is less than 1.30 volts, deposits may be produced with a current density greater than 1.20 amperes/square foot providing the current density does not exceed 4.0 amperes/square foot. In Runs 89 and 92, deposits were produced with a voltage of 1.25 volts and current density of 2.5 amperes/square foot. In Runs 25 and 30, deposits were produced with applied voltages of 1.30 volts with current densities respectively of 0.81 and 0.51 amperes/square foot. Current densities greater than 20 amperes/square foot break up the sodium zincate-urea-cellulose system throwing the cellulose to the top of the plating solution.

Out of 10 runs tried with nickel anodes and cathodes and nickel-copper pairs, deposits were produced in only two: With a nickel anode and cathode - 1.70 volts, 0.11 amperes/square foot; and with a copper cathode, nickel anode - 1.30 volts, 0.06 amperes/square foot. Attempts to reduplicate these two runs were unsuccessful. Nickel is not corroded by alkaline sodium zincate, nor was zinc deposited in any of the runs made using nickel electrode pairs. In the one successful deposition with a nickel anode and cathode, the cellulose film was removed very easily from the anode.

Zinc in contrast to copper and nickel was found to be a poor material for electrodes in an alkaline sodium zincate media. The sodium zincate attacks the zinc, and zinc anodes dissolve during the plating trial.

The data for all runs made using cellulose are presented in Table 1, regardless of whether the runs were successful in depositing cellulose or not. The unsuccessful runs more clearly define the strict control and limitations that must be placed on applied potential and current densities in order to plate cellulose successfully, which were discussed.

Table 2 summarizes the results for ash contents with respect to the acid treatment used for each run. Table 3, which shows the solid content of methanol used in the treatment of 3 of the deposits, gives a slight indication of the amount of mechanical loss during the methanol dipping.

PART II -

ELECTRODEPOSITION OF CARBOXYMETHYLCELLULOSE

CARBOXYMETHYLCELLULOSE

Jansen (6), and Heuser (4) originally demonstrated the formation of carboxymethylcellulose from alkali cellulose by the action of monochloracetic acid:

$$C_6H_9O_4ONa + ClCH_2COOH \longrightarrow NaCl + C_6H_9O_4OCH_2COOH$$

Sodium cellulose	Monochlor-acetic acid	Sodium chloride	Carboxymethyl-cellulose

Sakurada (13) showed that the sodium salt of carboxymethylcellulose was soluble in water. Brown and Houghton (1) coined the term "CMC" and explored the structure of carboxymethylcellulose.

The sodium carboxymethylcellulose used in these experiments was produced by the Virginia Cellulose Department of the Hercules Powder Company, Wilmington, Delaware. Two grades of the sodium salt were used and are described as follows:

Cellulose Gum, CMC, Medium Viscosity Grade
Cellulose Gum, CMC, High Viscosity Grade

The molecular formula of sodium carboxymethylcellulose is given by Emil Heuser (5) as follows:

$C_6H_9O_4OCH_2COONa$ Formula weight: 242

But sodium carboxymethylcellulose, like cellulose, has large molecular weights since it consists of "X" number of the formula units given above. Unlike cellulose which is bivalent, it is monovalent.

ANALYTICAL DATA

Analytical data for CMC are given in the following table:

ANALYSIS	MEDIUM VISCOSITY GRADE	HIGH VISCOSITY GRADE
*Average molecular weight	150,000	300,000
*Purity	99.5 %	99.5 %
*Sodium content	...... 6.98 to 8.5 %	
*Sulfated ash	..... 21.6 to 26.3 %	
Ash at 800° C.	17.43 %	18.16 %
Chlorine content	0.29 %	0.32 %
Sulfur content	Less than 0.002 %	Less than 0.002 %
Iron content	0.019 %	0.010 %

THEORETICAL

Sodium content	9.49 %
Carbon content	39.65 %
Hydrogen content	4.58 %
Oxygen content	46.28 %
	100.00 %
Theoretical ash content (Na_2O)	25.6 %

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In addition to the above analyses, the ash contents were determined on a majority of the CMC deposits produced. For particular information, other

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* - Data received from Hercules Powder Co. by private communication.

special determinations were made as follows:

(1) A neutralization number was determined on 5 grams of 1% medium viscosity CMC solution before a plating run (Run 63), and a second neutralization number was determined on 5 grams of the 1% medium viscosity CMC solution immediately after the same run. Results compare thusly:

	BEFORE RUN	AFTER RUN
pH of solution	7.4	9.4
Milliliters of 0.103 N HCl to bring to pH 7.0	0.10	0.22
Neut number (expressed as mgs KOH/gm)	0.12	0.26

(2) A test for the presence of oxygen in the cathodic microbubbles produced during Run 85 was made. The microbubbles were collected by using a small porcelain spatula to gather the suspension on the surface of the 1% high viscosity CMC plating bath. The suspension was placed in a small vial and about 50 milligrams of ferrous sulfate added and mixed by shaking. No color change in the ferrous sulfate was noted, indicating the absence of oxygen in the microbubbles.

(3) Oxygen analyses were made on high viscosity CMC and on a sample of the deposit produced during Run 85. Results were:

Oxygen content of hi vis CMC:	41.70 %	(weight percent)
Oxygen content of deposit:	42.16 %	" "

Neither of the two figures are corrected for the oxygen remaining in the Na_2O. Correction of the oxygen content for the CMC would yield a value of 46.39% compared to the theoretical of 46.28%. The higher oxygen content of the deposit indicates that oxidation of the deposit takes place during electrodeposition.

(4) Solubility tests were made. The method used and the results obtained are given in Table 8, appendix.

CMC SOLUTIONS

Since a 1% solution of cellulose was used for the sodium zincate-urea-cellulose system, a 1% solution of CMC was used arbitrarily for this study. Twenty grams of CMC were weighed and added to two liters of distilled water for each batch of solution prepared. Because of the slow dissolution of Na-CMC in water, all batches were permitted to stand for one week yielding clear, water-white sols. CMC solutions are stable for long periods.

EFFICIENCY OF CMC DEPOSITION

The relationships for the calculation of current efficiency for both grades of CMC have already been developed and are given as equations (C) and (D) on page 5.

The same mathematical relationship between current and efficiency, and between weight of deposition and efficiency holds for CMC as for cellulose. Current and efficiency have an inverse relationship, weight of deposition and efficiency have a direct relationship.

Values obtained for the plating runs made on medium viscosity CMC and on high viscosity CMC are given in Tables 4 and 5 respectively. For medium viscosity, efficiencies range from 0.13 to 0.21% and for high viscosity from 0.07 to 0.11% (or about half as much as for medium viscosity CMC). A possible relationship between current efficiency and weight of deposition is shown in Graph 7, appendix.

EQUATIONS FOR THE DEPOSITION OF CMC

A graphical plot (Graph 5) of voltage for current for the runs made with 1% medium viscosity CMC using copper anodes and cathodes yields the following linear equation:

(1) Current = (38.0 x voltage) – 48.0 where voltage is greater than 2.00 volts.

The expression is derived from the algebraic equation for a straight line:

$$y = mx + b$$

where y is the current in milliamperes, x is voltage in volts, m (the slope) is 38.0, and b is the intercept of -48.0.

By use of the same procedure for Graph 3 – Weight of deposition vs current for 1% medium viscosity CMC, two expressions are derived giving the relationship of current and weight of deposition:

(2a) Current = 0.350 weight which is valid to 56 milliamperes and 0.160 grams (2.74 volts by equation (1))

(2b) Current = 0.556 weight – 36.0 which is valid from 43 milliamperes and 0.140 grams (2.40 volts)

Application of the linear equation to Graphs 6 and 4 respectively yields the three corresponding equations for 1% high viscosity CMC:

(3) Current = 30.8 voltage - 37.0 where voltage is greater than 2.00 volts.

(4a) Current = 0.372 weight which is valid to 52 milliamperes and 0.140 grams (2.90 volts)

(4b) Current = 0.658 weight - 40.0 which is valid from 52 milliamperes and 0.140 grams

Substitution of (1) in (2a) or (2b) will give the relationship for voltage and weight of deposition. Similarly substitution of (3) in (4a) or (4b) will give the relationship for voltage and weight of deposition for 1% high viscosity CMC.

Comparison of the experimentally obtained data and results calculated by use of the foregoing six equations are made in Table 6. The percentile errors (not shown in the table) are as follows:

Equation (1): average deviation: 8.1 %
maximum: (-20.0 %
(+18.0 %

Equation (3): average deviation: 2.5 %
maximum: (- 2.3 %
(+ 9.0 %

Equations (2): average deviation: 7.2 %
maximum: (-16.4 %
(+ 7.9 %

Equations (4): average deviation: 3.7 %
maximum: (-2.1 %
(+10.0 %

In obtaining the average for equations (2), the values for Runs 65 (40.7%), 63 (37.7%), and 64 (27.0%) were excluded since these are beyond the 80.0% confidence level. Inclusion of these gives an average deviation of 13.0%.

MECHANICS OF THE ELECTRODEPOSITION OF CMC

In these experiments at all voltages greater than 2.0 volts, microbubbles of gas were released at the cathode. Microbubbles were not given off at 1.00 volt - the intermediate range (1.0 - 2.0 volts) has not been explored. A quantitative test of a suspension of the microbubbles, employing ferrous sulfate to indicate the presence of oxygen, has shown that these do not contain oxygen. Analysis has shown, also, that CMC is slightly alkaline and that as electrodeposition proceeds the alkalinity increases; analyses show the presence of sodium and of minute amounts of chlorine. Low concentrations of sodium hydroxide and sodium chloride, as well as sodium-CMC, in the plating bath are thereby indicated.

Mantell (9)*, in discussing the electrolysis of molten NaOH, states "Sodium and hydrogen are deposited at the cathode, oxygen at the anode", and gives the cell reactions:

$$2\ NaOH \rightleftharpoons 2\ Na^+ + 2\ OH^-$$
$$2\ Na^+ + 2\ H_2O \longrightarrow 2\ NaOH + H_2\uparrow$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$4\ OH^- \longrightarrow 2\ H_2O + O_2\uparrow$$

These may be expressed by electrochemical equations as:

$$2\ NaOH \rightleftharpoons 2\ Na^+ + 2\ OH^-$$
$$2\ H_2O \rightleftharpoons 2\ H^+ + 2\ OH^-$$
$$\left.\begin{array}{l} 2\ Na^+ + 2\ominus = 2\ Na \\ 2H^+ + 2\ominus = H_2\uparrow \end{array}\right)\ \text{at the cathode}$$
$$4\ OH^- + 4\oplus = 2\ H_2O + O_2\uparrow\ )\ \text{at the anode}$$

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* p. 528 ff.

Similarly the reactions for the electrolysis of sodium chloride are:

$$2\ NaCl \rightleftharpoons 2\ Na^+ + 2\ Cl^-$$

$$2\ Na^+ + 2\ominus = 2\ Na \qquad \text{) at the cathode}$$

$$2\ Cl^- + 2\oplus = Cl_2 \uparrow \qquad \text{) at the anode}$$

Weiser (15), in discussing Ostwald's characteristics of disperse colloidal systems, states "The arbitrary nature of the limits (of particles size) is evidenced by the fact that certain substances such as egg albumin and hemoglobin may be molecularly dispersed in water, but the molecules of the compounds are so large that they come well within the colloidal range". Heuser (5), in his text, recognizes the colloidal nature of cellulose and its derivatives, yet with reference to CMC says "The glycolic acid ethers of cellulose lend themselves to sale formation with alkalies..."

Thus, sodium CMC both possesses properties of salts and characteristics and properties of colloids. Salts, by modern theory, are those compounds which ionize in aqueous media. The large size, colloidal nature, and weak charge (since it is organic) of the CMC anion formed in water solution would cause it to be very immobile.

Assuming that the dominant mechanism in the deposition of CMC is due to the electrochemical properties of sodium, and by analogy to NaOH and NaCl, the electrochemical equations for the plating of CMC would be:

$$\text{(I)} \quad 4\ C_6H_9O_4OCH_2COONa \rightleftharpoons 4\ Na^+ + 4\ C_6H_9O_4OCH_2COO^-$$

$$\text{(II)} \quad 2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2 \uparrow$$

$$\text{(III)} \quad 2\ NaOH \rightleftharpoons 2\ Na^+ + 2\ OH^-$$

$$\text{(IV)} \quad 2\ H_2O \rightleftharpoons 2\ H^+ + 2\ OH^-$$

$$\left.\begin{array}{ll} (V) & 2\ C_6H_9O_4OCH_2COO^- + 2\ H^+ = 2\ C_6H_9O_4OCH_2COOH \\ & \qquad\qquad\qquad\qquad\qquad\qquad \text{(Deposits)} \\ (VI) & 2\ C_6H_9O_4OCH_2COO^- + 2\ Na^+ = 2\ C_6H_9O_4OCH_2COONa \\ & \qquad\qquad\qquad\qquad\qquad\qquad \text{(Deposits)} \\ (VII) & 4\ OH^- + 4\ \oplus = 2\ H_2O + O_2 \uparrow \end{array}\right)\text{ at the anode}$$

$$\left.\begin{array}{ll} (VIII) & 2\ Na^+ + 2\ \ominus = 2\ Na \\ (IX) & 2\ H^+ + 2\ \ominus = H_2 \uparrow \end{array}\right)\text{ at the cathode}$$

Equations (V), (VI), and (VII) are a simplification of the complex electrolytic oxidation taking place at the anode and producing the CMC deposition. The sodium most probably acts in a cyclic fashion passing through the successive stages of equations (II), (III), and (VIII) as deposition takes place - as sodium CMC is deposited by (VI), additional sodium ions are provided to the system by (I). That oxidation takes place is proved by the higher oxygen content of the deposited CMC as compared to CMC itself, and with copper electrodes no release of gas has been observed at the anode. Coupling, producing some polymerization, is among possible reactions taking part in the anodic complex.

The lower ash contents (see Table 7) of the anodically produced CMC deposits as compared to the ash content of CMC indicates that the dual electrochemical reactions of (V) and (VI) proceed simultaneously, but not with equal rate. For copper electrodes (VI) and (VIII) are the dominant reactions. For nickel electrodes, (V) and (VII) prevail as demonstrated by the lower ash content of the deposits and their lacelike appearance due to formation of oxygen bubbles at the anode.

The only ion not balanced exactly in the equations as given is that of sodium. Any excess in the number of sodium ions present would result in the reversal of equation (III) withdrawing hydroxyl ions from the solution - inhibiting the anodic release of oxygen - and accounting for the increase in alkalinity as electrodeposition proceeds.

The electrolysis of sodium chloride has been neglected in the suggested equations because of the small amount of chloride present. In a commercial process where the electrolyte would be continuously recycled, chloride would build up in concentration and if it became too high would become troublesome through its corrosive action on the cathode. Cathodes throughout these runs remained clean, free from corrosion, neither gained nor lost weight, and exhibited none of the effects attributable to chlorine action.

Kanning (7) points out that decomposition voltage varies with the nature of the electrodes and that excessive higher potentials (or overvoltages) are demanded with the liberation of a gas, particularly with cathodic release of hydrogen and anodic release of oxygen. Mantell (9) states that

> "It is difficult to regulate the electrode potential for any one reaction so that all oxygen at the anode or hydrogen at the cathode is absorbed by the depolarizer. The amount of oxidation or reduction is a function of the depolarizer, the current density at the anode or cathode (because of its influence on the rate of gas evolution), the concentration of the depolarizer, its diffusion, mechanical effects such as stirring, catalytic influence of added compounds, temperature, the nature of the anode material, and the solvent."

The electrochemical dissociation of sodium CMC, of NaOH, of water, the evolution of hydrogen, and under certain conditions of oxygen (nickel electrodes), and the other factors cited, all occurring in the CMC plating system contribute to the poor current efficiency found in these experiments.

Kanning (7) gives the Nernst equation in the following form:

$$E = E_o + \frac{0.0591}{n} \log C$$

> where E_o is the normal electrode potential, n is the number of electrons (equal to unity since CMC is monovalent), and C is the concentration in moles/liter.

A 1% solution of medium viscosity CMC has a molar concentration of 0.0000667; the normal potential for sodium is 2.712 volts, for hydrogen 0.000 volts, and for oxygen -1.229 volts. Totals for the cathode and anode will be:

Cathode: $E = 2.712 + (0.0591 \times -4.176) = 2.466$ volts

Anode: $E = -1.229 + (0.0591 \times -4.176) = -1.475$ "

Decomposition voltage: (Cathode - Anode) 0.991 volts

Experimentally, it was found that deposition of CMC does not occur below 1.0 volt.

The decomposition voltage for NaOH is 1.69 volts - it would therefore be anticipated that cathodic evolution of hydrogen would not take place in the CMC system at potentials lower than this value. No evolution was found at 1.0 volt, and but very little at 2.0 volts. Further, the "breaks" in Graphs 3 and 4 are in the neighborhood of the normal potential for sodium.

The foregoing values demonstrate the validity of the original assumption that the dominant mechanism in the electrodeposition of CMC is due to the electrochemical properties of sodium.

The striation lines produced in copper deposited CMC using potentials of 3.0 or more volts are probably caused by stresses from the electro-competition of the anodic reactions.

DETERMINATION OF OPTIMUM CONDITIONS

Three items are important in determination of the optimum conditions for the plating of CMC:

(1) Plots of individual runs made at different voltages for both grades, shown in Graphs 1 and 2. The runs made with applied potentials of greater than 3.0 volts show a definite slope when current is plotted against time - the current "falls off" as CMC is deposited, whereas runs made with potentials of less than 3.0 volts have relatively level plots of current versus time. In the latter currents and current densities are almost constant for the duration of the run; the currents and current densities are variable when the applied potential exceeds 3.0 volts.

(2) Current efficiencies as tabulated for both grades of CMC in Tables 4 and 5. The best efficiencies were obtained for both grades when the applied voltage was between 2.0 and 3.0 volts.

(3) Examination of the deposits produced reveals that those made with potentials up to 3.0 volts were smooth, those made with potentials above 3.0 volts containing striated lines - the lines becoming more numerous and more pronounced as the voltage rose.

The optimum range of potential for CMC deposition is therefore set at 2.50 to 3.00 volts, with currents of 42 to 66 milliamperes, and corresponding current densities of 0.47 to 0.75 amperes/square foot. The plots of the individual runs in Graphs 1 and 2 further indicate that current begins to fall off at all applied potentials after 12 to 15 minutes, thus 15 minutes is placed as the time of maximum duration for plating runs.

Copper has been found to be a satisfactory electrode material. CMC may be deposited on nickel as well as on copper, nickel electrodes, however, impart different characteristics to the electrolytically produced films. Nickel deposited films under low potentials have a gummy, non-drying characteristic, while those produced at higher potentials have a lacelike appearance due to the evolution of oxygen at the anode, the bubbles of which adhere to the electrode causing deposition around them.

Current efficiencies for the optimum conditions and copper electrodes are:

For medium viscosity CMC: 0.186 to 0.213 %

For high viscosity CMC: 0.084 to 0.098 %

SUMMARY OF DATA

Data for both grades of CMC are summarized in Tables 4 and 5 respectively for medium viscosity and high viscosity, and has been discussed in the preceeding section. Table 6 has been discussed and presents the comparison of experimentally obtained data and that calulated by the equations derived for the deposition of CMC.

Table 7 presents the ash contents for many of the CMC deposits produced. All of the ash contents are lower than the ash determined on the respective grade of CMC. Ash contents of nickel deposited CMC are lower than those of copper deposited films - this has previously been mentioned as one of the factors indicating the prevalence of one electrochemical equation over another in the mechanism of the deposition.

Only one CMC deposit was acid treated. CMC deposits are removed very readily and easily from the electrodes by peeling, and do not require acid treatment to effect their removal as do the deposits of cellulose from the sodium zincate-urea-cellulose system. The acid treatment, similarly to that of the acid treatment of cellulose deposits, reduces the ash content of the deposit probably by converting the sodium salt back to the acid form of CMC, and in addition makes the CMC deposit gummy and gelatinous in character. Since this was only a cursory examination no conclusions are being drawn, however, nickel deposited CMC and acid treated CMC possess the gummy, semi-solid characteristic, and nickel deposition and acid treatment - either together or singly - seem to offer interesting prospects for the production of films having many diverse characteristics and properties. Acid treatment for copper deposited CMC films produced over a wide range of potentials likewise should produce a final result with many varied characteristics.

The graphs plotted for CMC have been discussed, except for the last - Graph 8 (Power versus weight of deposition). This particular curve was plotted in an effort to accentuate the breaking point of Graph 3. It illustrates two additional points: (1) That the break (as in Graphs 3 and 4) is not sharply defined, but is a gradual change from one linear slope to another over a wide area; (2) That the total power requirement for the deposition of CMC is under 1.0 watt.

CMC deposits are soluble in 20% HCl almost instantly, are insoluble in methanol and 10% NaOH, and are very slightly soluble in water. Data on solubility is tabulated in Table 8.

PART III -

CELLULOSE VERSUS CARBOXYMETHYLCELLULOSE

CMC IN SODIUM ZINCATE-UREA-CELLULOSE

Runs 56, 57, and 58 were made using a bath consisting of:

75% of sodium zincate-urea-cellulose solution
25% of 1% medium viscosity CMC solution

with copper electrodes, immersed to 3.2 inches, set 1 inch apart, at 1.30 volts with an average current of 40 milliamperes. The current density was 0.44 amperes/square foot. Deposits were produced in all three runs, and zinc deposited on the copper cathode. Run 59 was made under the same conditions, but using a fresh mixture of the same proportions.

The deposits produced were treated with 20% HCl, were rinsed with water, methanol dipped, and air dried. The deposits lost fragments during the acid treatment, and when dried were very stiff and brittle, breaking very easily.

Cellulose requires potentials under 1.30 volts for optimum deposition; CMC requires potentials of 2.5 - 3.0 volts for optimum deposition (this was unknown at the time the above runs were made, the full study of CMC was made subsequently - all run numbers are in consecutive order relative to time), and very little CMC would be deposited at 1.30 volts. CMC deposits are also acid soluble, cellulose deposits require acid treatment.

Therefore, it may be concluded, because of the different requirements for cellulose and CMC, that carboxymethylcellulose is not a satisfactory additive for the sodium zincate-urea-cellulose system.

COMPARISON OF DEPOSITS

Any comparison of the deposits produced electrolytically from sodium zincate-urea-cellulose with those produced from 1% solutions of CMC, unfortunately at this time, must be largely visual. The small amounts of deposits produced from each system were sufficient only for a few chemical analysis; the amounts were such that testing by physical methods (i.e., tensile strength, permeability, dielectric strength) were precluded. However, certain characteristics have been noted:

Constitution - Deposits produced from sodium zincate-urea-cellulose appear to consist of minute fibers welded together by the solvent action of the sodium zincate-urea. CMC deposits are more like films - those produced under potentials of 1.0 - 3.0 volts are smooth and non-fibrous; those produced at higher voltages appear to be more crystalline in character (inferred from the striation lines).

Friability - Cellulose deposits are very friable, stiff, and brittle; those of CMC do not crumble readily into small fragments. although those produced above 3.0 volts are stiffer and possess a tendency toward brittleness.

Strength - Cellulose deposits are readily pulled apart into small pieces; CMC deposits appear to have greater strength.

Elasticity:- Cellulose deposits are non-elastic; CMC deposits possess some flexibility and a little elasticity.

Uniformity - CMC electrodeposition produces face deposits with little or no deposition on the back of the anode; cellulose deposits equally well on the face and back of anodes.

Heat stability - Cellulose deposits (after acid treatment) when dried at 105° C. shrivel and become brown to black in color; temperatures up to 105° C. do not appear to effect CMC films. The low ash of acid treated cellulose deposits, and the higher ash content of CMC films may be a factor in the heat stability of both types.

Shrinkage - Shrinkage in the air drying of CMC films is estimated at less than 10%, compared to an estimated 50% shrinkage in the drying of cellulose deposits.

Removal from anodes - The greatest apparent advantage of CMC electrodeposition over that of cellulose to the present time is the easier removal of CMC films from the anodes. Although CMC films will peel easily, they have a ready tendency to tear. Development of methods to remove either or both types in large sections from anodes is tantamount to their practical application.

Solubility - Solubilities of both types are given in Table 8. The insolubility of cellulose deposits in 20% HCl could be a definite advantage in applications where acid insolubility is important. Both types are insoluble in methanol, in 10% NaOH, and in water (CMC but slightly soluble).

Hazards - Sodium zincate-urea solution is corrosive to many metals, including copper upon prolonged exposure to the solvent, CMC solutions are not corrosive. Hydrogen released at the cathode in CMC deposition will be a problem in any future commercial process. Ammonia (and its corrosive action) will be a major problem in the storage of sodium zincate-urea, as well as ammonia vapors when the sodium zincate-urea is used in open plating baths.

CONTROL OF DEPOSITION

(1) Cellulose

The narrow range of applied potential through which cellulose is deposited from the sodium zincate-urea-cellulose system makes electrical control difficult. It was found in this study, that as cellulose deposits the circuit requires constant adjustment of the variable rectifier to hold the potential constant, the current and current density fall off as deposition proceeds. Cozzarelli, in his original study, had similar experiences - the current (and current density) in the original work was maintained at a constant value, the applied potential thereby varied; continuous adjustment had to be made to maintain a constant current. Cozzarelli reported this in detail.

(2) CMC

CMC as indicated by the plots in Graphs 1 and 2, is very easily controlled, the initial setting of the rectifier to give a particular potential requires no further adjustment as deposition proceeds. The current, when the applied potential exceeds 3.0 volts, will fall off - the extent to which this occurred may be seen by examination of the data for each run included as the final part of the appendix of this report. The wide range over which CMC will deposit in contrast to that of cellulose, even if the variances in current were greater than found, simplifies the problem of control - variances may be tolerated, in cellulose deposition variances must be prohibited. The potential spread for cellulose is 0.18 volts as maximum, for CMC 0.50 volts and greater is permissible. The cellulose system is highly sensitive, the CMC system is not.

CONDUCTIVITIES OF SOLUTIONS

In many electrochemical processes, determination of the concentrations of the electrolytes are made by measurement of the conductivities. The few measurements that have been made during these experiments are listed in Table 9, and are so presented for information.

One aspect of conductivity - as a means of determining whether or not a complex is formed in the sodium zincate-urea-cellulose system - has been discussed (page 17).

CONCLUSIONS

ELECTRODEPOSITION OF CELLULOSE

The results of Cozzarelli's original work (2) have been verified, with the sole exception that in the present study zinc was found to deposit on the cathode at all potentials and current densities within the range of the optimum conditions for cellulose deposition.

Analytical methods have shown that sodium zincate-urea deposits with the cellulose; values for the contents of urea and cellulose calculated from the ash content and nitrogen analyses agree with the ultimate analyses of the deposit for carbon, hydrogen, and oxygen. The hydrogen content by analysis is higher than that calculated and is taken to indicate the presence in small amounts of sodium bicarbonate in the deposit as a result of the reaction of urea in alkaline media to break down into ammonia and sodium carbonate. It has not been determined whether sodium zincate and urea co-deposit with the cellulose, or are entrapped in the cellulose during deposition, or are deposited as part of a sodium zincate-urea-cellulose complex. The analytical data obtained give credence to the formation and deposition of a complex; electrodeposition of cellulose is felt to be a dual mechanism of the co-deposition of sodium zincate-urea with cellulose, and the deposition of a complex, which would explain the differences found in the various plating trials made.

It has been found that zinc is not a satisfactory metal for the electrodes. Nickel electrodes, the use of which makes the removal of cellulose deposits easier and prohibits the cathodic deposition of zinc, are of doubtful value since only 1 run out of 8 using them produced a cellulose deposit.

The use of strong acid solutions (above 25%) to treat the deposits results in the partial mechanical destruction of the deposits by the gas evolved from the chemical reaction between the acid and components in the deposit. Use of 20% solutions of acetic, hydrochloric, and nitric acids to treat the deposits have proven more satisfactory than more highly concentrated acid solutions, although there is still some mechanical loss. In order to produce a cellulose deposit having low ash contents, it is necessary to treat the deposit for 10 minutes or longer using 20% HCl or 20% HNO_3.

Use of current efficiencies for the cellulose system are questionable, because of the residual sodium zincate and urea present in the cellulose deposit. It is suggested that this can be overcome by specifying the acid treatment and the ash content of the deposit when expressing the efficiency of the deposition.

ELECTRODEPOSITION OF CMC

The optimum conditions for the electrodeposition of carboxymethylcellulose films have been determined for 1% solutions of medium viscosity and high viscosity CMC. Copper has been found to be a suitable electrode material. Nickel electrodes may also be used, but dependent upon the applied potential, produce films having different characteristics from those produced on copper electrodes.

The electrochemical equations for the deposition of CMC have been suggested. Mathematical relationships for current and voltage, and for current and weight of deposition have been derived by graphical plot of the data obtained, comparison of data calculated from these equations with the experimental data has an average deviation of 8% - with a few single values reaching a maximum of plus or minus 20%.

Acid treatment is not required to remove CMC deposits from the anodes - acid treatment has been found to change the character of the deposits and offers possibilities (with use of copper or nickel electrodes) of being able to obtain films with many different characteristics and properties. Care must be exercised here, however, since it has been determined that CMC deposits are soluble in 20% HCl. CMC deposits are insoluble in methanol, and in 10% NaOH, and are very slightly soluble in water.

CMC electrodeposition, in contrast to cellulose deposition, produces only face deposits - very little or no deposition takes place on the back of the anode. CMC deposits have been compared using visual observation with those of cellulose. It has further been shown that the cellulose system is highly sensitive, the CMC system is not - cellulose deposition accordingly requires very close and rigid control to produce deposits, the CMC system (although it has not been necessary) will tolerate greater fluctuations and variances in applied potential and in current density.

CONCLUSIONS

OPTIMUM CONDITIONS FOR DEPOSITION

The optimum conditions for the electrodeposition of cellulose and both grades of CMC are as follows:

	CELLULOSE	MED VIS CMC	HI VIS CMC
Applied potential: (volts)			
Minimum	1.10	2.50	2.50
Maximum	1.28	3.00	3.00
Current (milliamperes):			
Minimum	11	42	42
Maximum	120	66	66
Current density (amps/sqft):			
Minimum	0.13	0.47	0.47
Maximum	1.10	0.75	0.75
Power requirement (watts):			
Minimum	0.012	0.100	0.100
Maximum	0.155	0.200	0.200
Current efficiency (%):			
Minimum	0.80	0.186	0.084
Maximum	5.53	0.213	0.098
Plating time (minutes)			
Maximum	15	15	15
Weight deposited (grams on 0.089 sqft)*			
Minimum	0.035	0.111	0.111
Maximum	0.451	0.172	0.144
Electrodes - best	copper	copper	copper
Nickel	doubtful	usable	usable
Zinc	no good	——	——
Electrode distance			
Minimum	1.0 cm	1.0 cm	1.0 cm
Maximum	1.0 inch	1.0 inch	1.0 inch

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* - Weights given are those which are deposited under the conditions of applied potential and current density specified above. The weights for cellulose are for acid treated deposits, ash content less than 4.0%.

CONCLUSIONS

On the basis of the optimum conditions, it is concluded that CMC is not a satisfactory additive for the cellulose system, since the optimum conditions for the deposition of each is so different, as well as the fact that CMC is acid soluble and cellulose requires acid treatment.

FUTURE WORK

There are several phases which need further investigation, and others which have not been touched upon in either Cozzarelli's or the present study.

(1) The use of multiple electrodes, where every other is an anode and those between cathodes. Such use, by producing both face and back deposits of CMC should improve CMC efficiency. In the cellulose system, it should result in a net reduction of current density providing for better control.

(2) Distances between electrodes have only had a cursory examination, and the relationship of electrode spacing to efficiency should be found.

(3) The effects of mechanical stirring and temperature. Mechanical stirring in the cellulose system would have to be very slow and gentle because of the delicate nature of the deposits. Temperature readings should be made of the plating bath during runs to determine its effect, and by placing the plating bath in a second bath which is temperature controlled the temperature variable can be fully explored.

(4) Further study of the acid treatment of the deposits in both systems. In cellulose system, weaker acids should be used, and time as a function of acid treatment determined. In the CMC system, it has been indicated that

acid treatment might produce films of many different characteristics.

(5) Development of methods for removing large sections of deposits from the anodes is felt to be the most important phase of future study.

(6) Findings under (5) above would permit further investigation into the physical properties of the deposits for both systems. Physical characteristics will largely determine whether or not there are practical applications for cellulose and CMC electrodeposition.

(7) Further investigation into the mechanisms of the deposition of cellulose is felt necessary before marked improvements in current efficiency will be realized.

(8) An economic study into the cost of producing the sodium zincate-urea-cellulose solution compared to the costs of CMC solutions.

(9) Determination of the optimum conditions for CMC solutions of other than 1% concentration. 1% solutions may not necessarily be the optimum solution.

(10) A study of the potential hazards and methods for their control should also be undertaken.

(11) Concurrent with (7) above, the mathematical relationships for the cellulose system will have to be determined with the chemical.

Many of the above phases may be combined into a single study, or what might be better a group undertaking studies of the suggested phases at one time......

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APPENDIX A

EQUIPMENT

Details of the electrical equipment used are as follows:

(1) The rectifier:

Made by: Richardson-Allen Corp., New York
Title: "Double Unit Variable Plater"

A.C. Input	D.C. Output
115 Volts	6 / 12 Volts
18 Amperes	150 / 75 Amperes
1 Phase	Continuous duty
50-70 Cycles	105°F Ambient temp.

(2) Volt-Ammeter:

Made by: Weston Instrument Corp., Newark, N.J.
Title: "Weston D. C. Volt-Ammeter, Model 1"
Serial Number: 60340 Tested: March 3, 1954

(3) Triplett Meter:

Made by: Triplett Electrical Instrument Co., Bluffton, Ohio.
Title: "Triplett Volt-Ohm-Mil-Ammeter, Model 2405A"

(4) Conductivity Bridge:

Made by: Arthur H. Thomas Co., Philadelphia
Title: "Surfass Conductivity Bridge"
Used with a clear Platinum Electrode

APPENDIX B

TABLE 1. - Summary of Runs Made on the Electrodeposition of Cellulose.

RUN	ELECTRODE MATERIAL	D.C. VOLTAGE	D.C. CURRENT	CURRENT DENSITY	TIME OF RUN	CATHODE DEPOSIT	ANODE DEPOSIT	CURRENT EFFICIENCY (And/or Remarks)
		Volts	Milliamps	Amps/Sqft	Minutes	Grams	Grams	Percent
1	Cu and Cu	6.00	20,000	225.0	2	(Zinc)	———	(Solution broken)
2	Cu and Cu	1.00	2,000	22.50	5	(Zinc)	———	(Solution broken)
3	Cu and Cu	1.00	1,000	11.24	10	———	———	No deposit formed
4	Cu and Cu	2.20	500	5.62	10	(Zinc)	———	Deposit sloughed off anode
5	Cu and Cu	2.00	200	2.25	10	(Zinc)	———	Deposit sloughed off anode
6	Cu and Cu	1.30	110	1.24	10	(Zinc)	———	Deposit sloughed off anode
7	Cu and Cu	0.022	440	4.95	10	(Zinc)	———	Deposit sloughed off anode
8	Cu and Cu	0.023	460	5.17	10	———	———	No deposit formed
9	Cu and Cu	0.049	975	10.95	10	———	———	No deposit formed
10	Cu and Cu	0.011	2,250	25.30	10	———	———	No deposit formed
11	Cu and Cu	0.014	283	3.18	10	———	———	No deposit formed
12	Cu and Cu	1.20	43	0.48	15	(Zinc)	———	Cellulose deposit obtained
13	Cu and Cu	1.18	20	0.225	15	(Zinc)	———	Cellulose Deposit obtained
14	Cu and Cu	1.20	38	0.43	15	(Zinc)	———	Cellulose deposit obtained (Saved for analysis)
15	Cu and Cu	1.25	90	1.01	15	(Zinc)	———	Cellulose deposit obtained (Saved for analysis)
16	Cu and Cu	1.12	11	0.124	15	(Zinc)	———	Light deposit (anode)
17	Cu and Cu	1.20	50	0.56	15	(Zinc)	———	Heavy deposit (anode)
19	Cu and Cu	1.20	42	0.47	15	(Zinc)	———	Heavy deposit (anode)
20	Cu and Cu	1.30	40	0.45	10	(Zinc)	———	No deposit, solution 3 months old
21	Cu and Cu	1.22	50	0.56	10	(Zinc)	———	(Ditto for Run 20)
22	Cu and Cu	1.28	60	0.67	15	(Zinc)	———	Cellulose deposit (anode)
23	Cu and Cu	1.23	60	0.67	15	0.047	0.035*	0.25
24	Cu and Cu	1.25	70	0.79	15	0.057	0.050*	0.31
25	Cu and Cu	1.30	72	0.81	15	0.049	0.337	2.01
26	Cu and Cu	1.25	55	0.62	15	0.047	0.053*	0.41
27	Cu and Cu	1.20	28	0.32	10	0.021	0.058*	1.33
28	Cu and Cu	1.28	68	0.76	10	0.036	0.063*	0.60
29	Cu and Cu	1.28	50	0.56	12	0.035	0.151*	1.62
30	Cu and Cu	1.30	45	0.51	10	0.035	2.162 0.047*	(30.95 on total)" 0.67
31	Cu and Cu	1.25	40	0.45	10	0.023	4.130 0.054*	(28.3 on zinc) 0.87
32	Cu and Cu	1.27	40	0.45	10	0.024	2.444 0.051*	(39.36 on total)" 0.82
33	Cu and Cu	1.27	40	0.45	15	0.033	3.642 0.312*#	(39.08 on total)" 3.35
34	Cu and Cu	1.28	50	0.56	15	0.042	4.251 0.371*#	(36.48 on total)" 3.18

* - Weight of cellulose after acid treatment.
\# - Treated with dilute acid (5-10%).
" - Efficiency calculated using total weight of deposit which includes deposited alkali, urea, and cellulose before acid treatment.

TABLE 1. - Summary of Runs Made on the Electrodeposition of Cellulose
(Continued)

RUN	ELECTRODE MATERIAL	D.C. VOLTAGE	D.C. CURRENT	CURRENT DENSITY	TIME OF RUN	CATHODE DEPOSIT	ANODE DEPOSIT	CURRENT EFFICIENCY (And/or remarks)
		Volts	Milliamps	Amps/Sqft	Minutes	Grams	Grams	Percent
35	Cu and Cu	1.28	60	0.67	15	0.036	3.355 0.312*#	(24.00 on total)" 2.23
41	Ni$^{=}$, Cu	2.10	58	0.65	15	———	———	No deposits formed
42	Cu$^{=}$, Ni	1.30	5	0.056	10	0.002	1.288	(74.00 on total)"
43	Ni and Ni	1.70	10	0.112	15	0.001	2.253	(96.50 on total)"
44	Ni and Ni	1.25	1.0	0.011	15	———	———	No deposits formed
45	Ni and Ni	1.80	12	0.135	10	———	———	No deposits formed
46	Cu and Cu	1.30	50	0.56	10	(Zinc)	———	Deposit sloughed off anode
47	Cu and Cu	1.30	30	0.34	10	(Zinc)	———	Deposit sloughed off anode
48	Cu and Cu	1.27	35	0.39	15	0.030	4.741 0.451*#	(58.14 on total)" 5.53
49	Ni and Ni	2.15	78	0.88	15	———	———	No deposits formed
50	Ni and Ni	1.80	38	0.43	10	———	———	No deposits formed
50A	Ni and Ni	1.80	40	0.45	10	———	———	No deposits formed
51	Cu and Cu	1.25	50	0.56	10	0.030	3.546 0.055*#	(45.67 on total)" 0.71
52	Cu and Cu	1.30	55	0.62	15	0.044	0.323*#	2.52
53	Ni and Ni	1.93	10	0.112	15	———	———	No deposits formed
54	Cu$^{=}$, Ni	1.98	40	0.45	15	———	———	No deposits formed
89	Cu and Cu	1.25	220	2.47	10	0.039	3.272 0.417*#	(9.58 on total) 0.54
90	Cu and Cu	1.00	2.4	0.027	15	0.004	0.011	Very little deposit
91	Zn and Zn	0.14	235	2.64	15	0.078	(Zinc) -0.074	0.074 gms Zn were lost from anode, no cellulose deposit
92	Cu and Cu	1.25	220	2.47	10	0.032	3.185 0.433*#	(9.32 on total) 0.56
	The following runs were made using sodium zincate-urea without cellulose in solution:							
18	Cu and Cu	1.20	48	0.54	15	0.0085	-0.0100	Anode lost copper
36	Cu and Cu	1.25	10	0.112	10	0.005	-0.003	(Residual voltage 1.10 V)
37	Ni and Ni	1.27	3	0.034	10	-0.0010	0.000	(Residual voltage 0.20 V)
38	Ni$^{=}$, Cu	1.25	40	0.45	10	0.005	-0.024	(Residual voltage 1.10 V)
39	Cu$^{=}$, Ni	1.25	10	0.112	10	0.0010	-0.0010	(Residual voltage 0.20 V)
40	Zn$^{=}$, Cu	1.25	32	0.36	10	0.012	-0.016	(Residual voltage 1.15 V)

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* - Weight of cellulose after acid treatment.
# - Treated with dilute acid (5-10%).
" - Efficiency calculated using total weight of deposit which includes deposited alkali, urea, and cellulose before acid treatment.

TABLE 2. - Ash contents of treated cellulose deposits.

In the following table, the weight of deposit given is the weight after the specified treatment. The ash content at 800° C. was obtained on the treated deposit. The weight of deposit is in grams.

RUN	WEIGHT DEPOSIT	PERCENT ASH	TREATMENT USED FOR DEPOSIT
14) 15)	(Combined)	46.85	Deposits air dried, scraped from anodes, broken up into fine particles. Not acid treated.
22) 24)	0.050	9.33	Treated in 20% acetic acid for 15 minutes, water rinsed, air dried, scraped from anodes, combined.
23	0.035	8.86	Treated in 20% acetic acid for 15 minutes, water rinsed, air dried.
25	0.337	64.9	Rinsed with water, air dried. Not acid treated.
26	0.053	3.40	Treated in 20% HCl for 10 minutes, water rinsed, air dried.
27	0.058	1.22	Treated in 20% HCl for 10 minutes, water rinsed, scraped off anode, then left to air dry.
28	0.063	33.98	Treated in 20% HCl for 5 minutes, water rinsed, air dried, then scraped from anode.
29	0.151	2.37	Treated in 20% HCl for 10 minutes, water rinsed, air dried, then scraped from anode.
30	0.046	3.90	Treated by dipping in 50% HCl, then methanol, peeled from anode, air dried.
31	0.054	2.89	Treated in 20% HCl for 10 minutes, water rinsed, methanol dipped, air dried.
32	0.051	21.49	Treated in 20% HCl for 5 minutes, water rinsed, methanol dipped, air dried.
33	0.312	9.58	20% acetic acid for 12 minutes, water rinsed, air dried.
34	0.371	2.09	Dipped in 5% HCl, 10 minutes in 20% HNO_3, water rinsed, methanol dipped, air dried.
35	0.312	12.37	Treated in 20% HNO_3 for 5 minutes, water rinsed, methanol dipped, air dried.

TABLE 2. - Ash contents of treated cellulose deposits.
(Continued)

RUN	WEIGHT DEPOSIT	PERCENT ASH	TREATMENT USED FOR DEPOSIT
48	0.451	2.44	Treated in 20% HNO_3 for 10 minutes, water rinsed, methanol dipped, air dried.
51	0.055	2.20	Treated in 20% HCl for 10 minutes, water rinsed, methanol dipped, air dried.
52	0.323	3.15	Treated in 20% HCl for 10 minutes, water rinsed, methanol dipped, air dried.
89	0.417	1.86	Treated in 20% HCl for 10 minutes, water rinsed, methanol dipped, air dried.
92	0.433	2.07	Treated in 20% HCl for 10 minutes, water rinsed, methanol dipped, air dried.

Percentages given for all acids in the above table are by volume.

TABLE 3. - Solids content of methanol used in treating deposits.

15.0 milliliters of the methanol used in treating the deposits from Runs 30, 31, and 32 were weighed, evaporated on a steam bath, oven dried at 105° C., cooled and reweighed.

Solid Content: 0.72 % (by weight)

TABLE 4. - Summary of Runs made on the electrodeposition of 1% solution of medium viscosity carboxymethylcellulose.

RUN	ELECTRODE MATERIAL	D.C. VOLTAGE	D.C. CURRENT	CURRENT DENSITY	TIME OF RUN	WEIGHT DEPOSIT	EFFICIENCY
		Volts	Milliamps	Amps/sqft	Minutes	Grams	Percent
55	Cu and Cu	3.00	20	0.225	10	0.085	0.203
60	Cu and Cu	3.00	57	0.64	15	0.170	0.213
61	Cu^{-}, Brass screen anode	3.00	62	0.69	15	0.118	0.136
62	Cu^{-}, Ni	3.00	52	0.57	15	0.112	0.154
63	Cu and Cu	3.00	65	0.73	15	0.114	0.122
64	Cu and Cu	4.00	123	1.43	15	0.320	0.186
65	Cu and Cu	2.00	28	0.31	15	0.135	0.135
66	Cu and Cu	1.00	3.0	0.034	15	0.008	0.191
67	Cu and Cu	2.00	25	0.29	15	0.069	0.197
68	Cu and Cu	2.50	42	0.47	15	0.111	0.189
69	Cu and Cu	3.00	65	0.73	15	0.172	0.189
70	Cu and Cu	3.50	77	0.87	15	0.203	0.188
71	Cu and Cu	4.00	105	1.19	15	0.253	0.172
72	Cu and Cu	5.00	142	1.61	15	0.320	0.161
73	Cu and Cu	2.60	55	0.62	15	0.162	0.211
74	Cu and Cu	2.60	58	0.65	15	0.163	0.201
75	Cu and Cu	2.80	65	0.73	15	0.171	0.188
76	Cu and Cu	3.50	79	0.89	15	0.200	0.181
77	Ni and Ni	3.50	96	1.05	15	0.185	0.138

Runs 55, 60 through 65:	Lot A, 1% medium viscosity carboxymethylcellulose
Runs 66 through 72:	Lot B, 1% medium viscosity carboxymethylcellulose
Runs 73 through 77:	Lot C, 1% medium viscosity carboxymethylcellulose

TABLE 5. - Summary of runs made on the electrodeposition of 1% solution of high viscosity CMC.

RUN	ELECTRODE MATERIAL	D.C. VOLTAGE	D.C. CURRENT	CURRENT DENSITY	TIME OF RUN	WEIGHT DEPOSIT	EFFICIENCY
		Volts	Milliamps	Amps/sqft	Minutes	Grams	Percent
78	Cu and Cu	2.00	25	0.28	15	0.074	0.106
79	Cu and Cu	2.50	41	0.46	15	0.111	0.097
80	Cu and Cu	2.80	50	0.57	15	0.134	0.096
81	Cu and Cu	3.00	54	0.62	15	0.142	0.094
82	Cu and Cu	3.50	73	0.84	15	0.171	0.084
83	Cu and Cu	4.00	84	0.96	15	0.188	0.080
84	Cu and Cu	5.00	117	1.32	15	0.241	0.074
85	Cu and Cu	2.72	51	0.57	15	0.137	0.096
86	Cu and Cu	1.00	2.4	0.028	15	0.003	0.045
87	Ni and Ni	2.70	48	0.54	15	0.113	0.084
88	Ni and Ni	3.00	55	0.62	15	0.144	0.094

Runs 78 through 88: Lot D, 1% high viscosity CMC

TABLE 6. - Comparison of experimental and calculated values for current and weight of deposition of carboxymethylcellulose based on voltage.

The values tabulated for the calculated current, and calculated weights of deposition were obtained by use of the equations for the deposition of CMC derived from the plots of the experimental data. There are two lists of values for "calculated weight of deposition" - the first column is calculated from the voltage, the second is calculated from the measured experimental current.

	D.C.	D.C. CURRENT		WEIGHT OF DEPOSITION		
RUN	VOLTAGE	Experimental Current	Calculated from voltage	Experimental weight obtained	Calculated from voltage	Calculated from experimental current
	Volts	Milliamperes	Milliamperes	Grams	Grams	Grams
For 1% medium viscosity CMC:						
60	3.00	57	66	0.170	0.183	0.163 (2a) 0.167 (2b)
63	3.00	65	66	0.114	0.183	0.182
64	4.00	123	104	0.320	0.252	0.286
65	2.00	28	28	0.135	0.080 (2a)	0.080 (2a)
66	1.00	3.0	(DNA)	0.008	0.009 (2a)	0.009 (2a)
67	2.00	25	28	0.069	0.080 (2a)	0.071 (2a)
68	2.50	42	47	0.111	0.134 (2a)	0.140 (2b) 0.120 (2a)
69	3.00	65	66	0.172	0.183	0.182
70	3.50	77	85	0.203	0.218	0.203
71	4.00	105	104	0.253	0.252	0.254
72	5.00	142	142	0.320	0.320	0.320
73	2.60	55	51	0.162	0.146 (2a) 0.156 (2b)	0.157 (2a) 0.163 (2b)
74	2.60	58	51	0.163	0.146 (2a) 0.156 (2b)	0.169 (2b)
75	2.80	65	58	0.171	0.169	0.182
76	3.50	79	85	0.200	0.218	0.207
For 1% high viscosity CMC:						
78	2.00	25	25	0.074	0.067 (4a)	0.067 (4a)
79	2.50	41	40	0.111	0.108 (4a)	0.110 (4a)
80	2.80	50	49	0.134	0.132 (4a)	0.134 (4a)
81	3.00	54	55	0.142	0.145 (4a) 0.144 (4b)	0.148 (4a) 0.143 (4b)
82	3.50	73	71	0.171	0.169	0.172
83	4.00	84	86	0.188	0.192	0.188
84	5.00	117	117	0.241	0.239	0.239
85	2.72	51	47	0.137	0.126 (4a)	0.137 (4a)
86	1.00	2.4	(DNA)	0.003	0.006 (4a)	0.006 (4a)

DNA - Does not apply; equations developed for calculation of current from voltage are for 2.0 volts and up.

Equation (2a): Current = 0.350 weight — valid to 56 milliamps and 0.160 grams (2.74 volts)

Equation (2b): Current = 0.556 weight - 36.0 — valid from 43 milliamps and 0.140 grams (2.40 volts)

Equation (4a): Current = 0.372 weight — valid to 52 milliamps and 0.140 grams (2.89 volts), for high viscosity CMC

Equation (4b): Current = 0.658 weight - 40.0 — valid from 52 milliamps and 0.140 grams (2.89 volts), for high viscosity CMC

Note: Where equations have not been indicated in the table, (2b) or (4b) respectively have been used for medium viscosity CMC and high viscosity CMC for the calculation of the weight of deposition.

TABLE 7. - Ash contents of CMC deposits.

RUN	ELECTRODE MATERIAL	VOLTAGE (Volts)	CURRENT (Milliamps)	TYPE OF CMC	WEIGHT PERCENT OF ASH AT 800° C.
Medium Viscosity CMC					17.43
60	Cu and Cu	3.00	57	med vis	14.90
62	Cu^-, Ni	3.00	62	med vis	2.96
63	Cu and Cu	3.00	65	med vis	0.46 (acid treated)
64	Cu and Cu	4.00	123	med vis	16.58
65	Cu and Cu	2.00	28	med vis	17.24
67	Cu and Cu	2.00	25	med vis	16.12
68	Cu and Cu	2.50	42	med vis	13.32
69	Cu and Cu	3.00	65	med vis	14.60
70	Cu and Cu	3.50	77	med vis	13.90
71	Cu and Cu	4.00	105	med vis	13.20
72	Cu and Cu	5.00	142	med vis	14.02
73	Cu and Cu	2.60	55	med vis	15.91
75	Cu and Cu	2.80	65	med vis	15.41
76	Cu and Cu	3.50	79	med vis	17.00
77	Ni and Ni	3.50	96	med vis	11.62
High viscosity CMC					18.16
80	Cu and Cu	2.80	50	hi vis	14.71
81	Cu and Cu	3.00	54	hi vis	15.40
82	Cu and Cu	3.50	73	hi vis	14.26
85	Cu and Cu	2.72	51	hi vis	15.21
87	Ni and Ni	2.70	48	hi vis	10.59
88	Ni and Ni	3.00	55	hi vis	11.68
84	Cu and Cu	5.00	117	hi vis	16.07

TABLE 8. - Solubilities of cellulose and CMC deposits.

To determine solubility, about 10 milligrams of deposit were weighed into small vials and 5.0 ml of solvent added, then left stand for 4 hours. Solvent was rinsed out with distilled water, vial with residue (except for cellulose) was dried at 105° C and reweighed when cool. The cellulose deposits were acid treated and air dried prior to solubility determinations, and it was found that these were not stable at 105° C and had to be dried by placing in a desiccator for several hours.

DEPOSIT	METHANOL	WATER	20% HCl	10% NaOH
Cellulose (acid treated)	Insoluble	Insoluble	Insoluble	Insoluble
Medium viscosity CMC:				
on copper electrodes	Insoluble	6.9 %	Soluble	Less than 1%'
on nickel electrodes	Insoluble	Insoluble	Soluble*	Less than 1%
High viscosity CMC:				
on copper electrodes	Insoluble	2.2 %	Soluble	Less than 1%'
on nickel electrodes	Insoluble	Insoluble	Soluble*	Less than 1%

' - NaOH causes swelling of CMC deposits regardless of type or electrode material. In copper deposited CMC, the NaOH becomes tinged with a slight green color due to removal of traces of copper from the deposit.

* - Nickel deposited CMC takes 2 or more hours to dissolve completely, while copper deposited CMC dissolves completely in less than 5 minutes.

TABLE 9. - Conductivities and resistances of solutions.

Conductivity was measured using a Surfass conductivity bridge with a clear platinum electrode (1 cm^2 cross section).

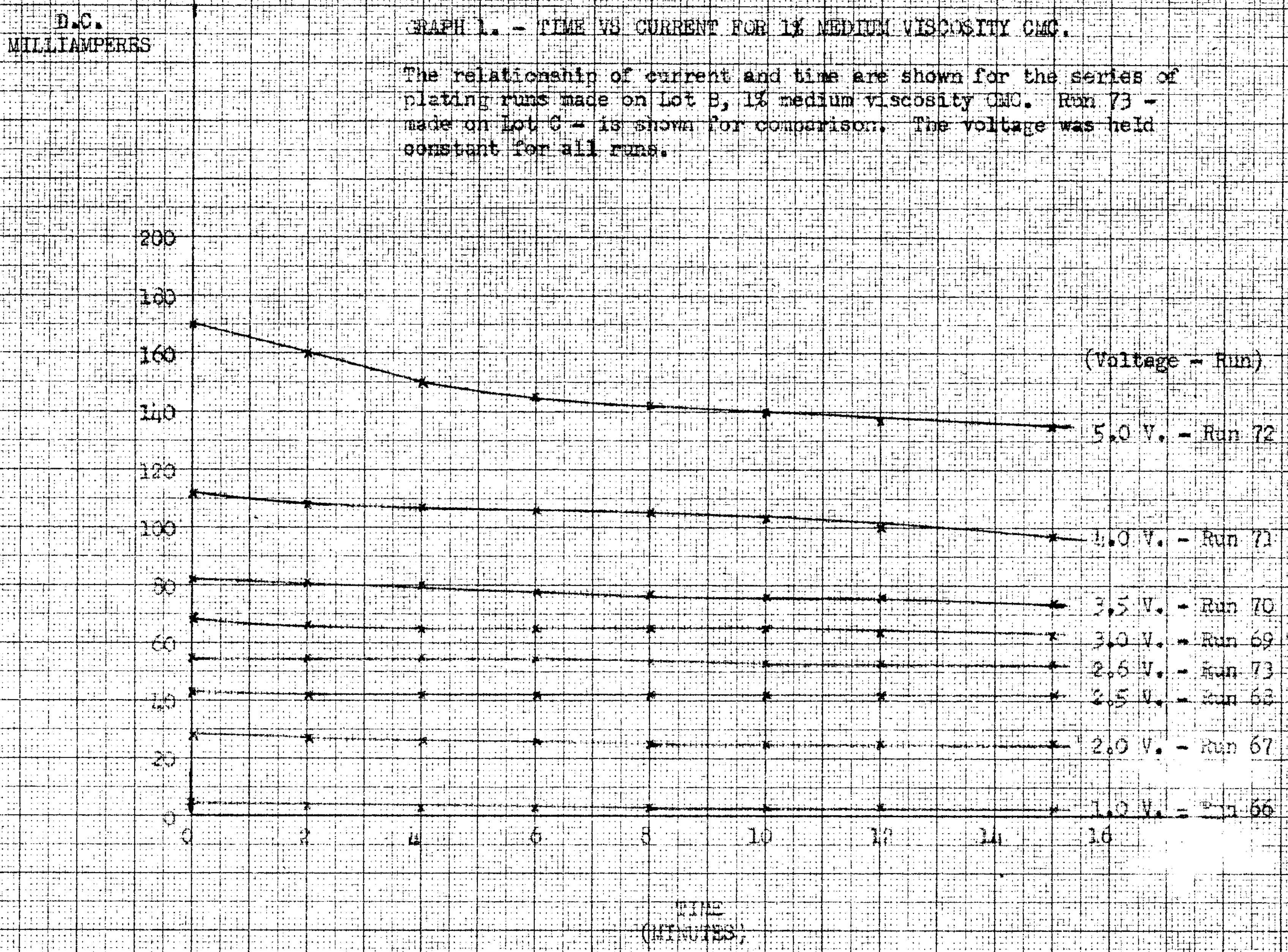
Resistance was measured using the Triplett meter and the regular copper anode and cathode in the plating bath.

SOLUTION	CONDUCTIVITY (at 25°C)	RESISTANCE
	Micromhos/cm	Ohms
Distilled water	3.0	
Tap water	(approx.) 200	
10% sodium hydroxide	160,000	
Sodium zincate-urea	66,000	
Sodium zincate-urea-cellulose	68,000	
Fresh 1% medium viscosity CMC (before Run 63)	1,780	370
Used 1% medium viscosity CMC (after Run 63)	1,680	400
Fresh 1% high viscosity CMC (before Run 81)	1,700	450
Used 1% high viscosity CMC (after Run 81)	1,620	490

APPENDIX C

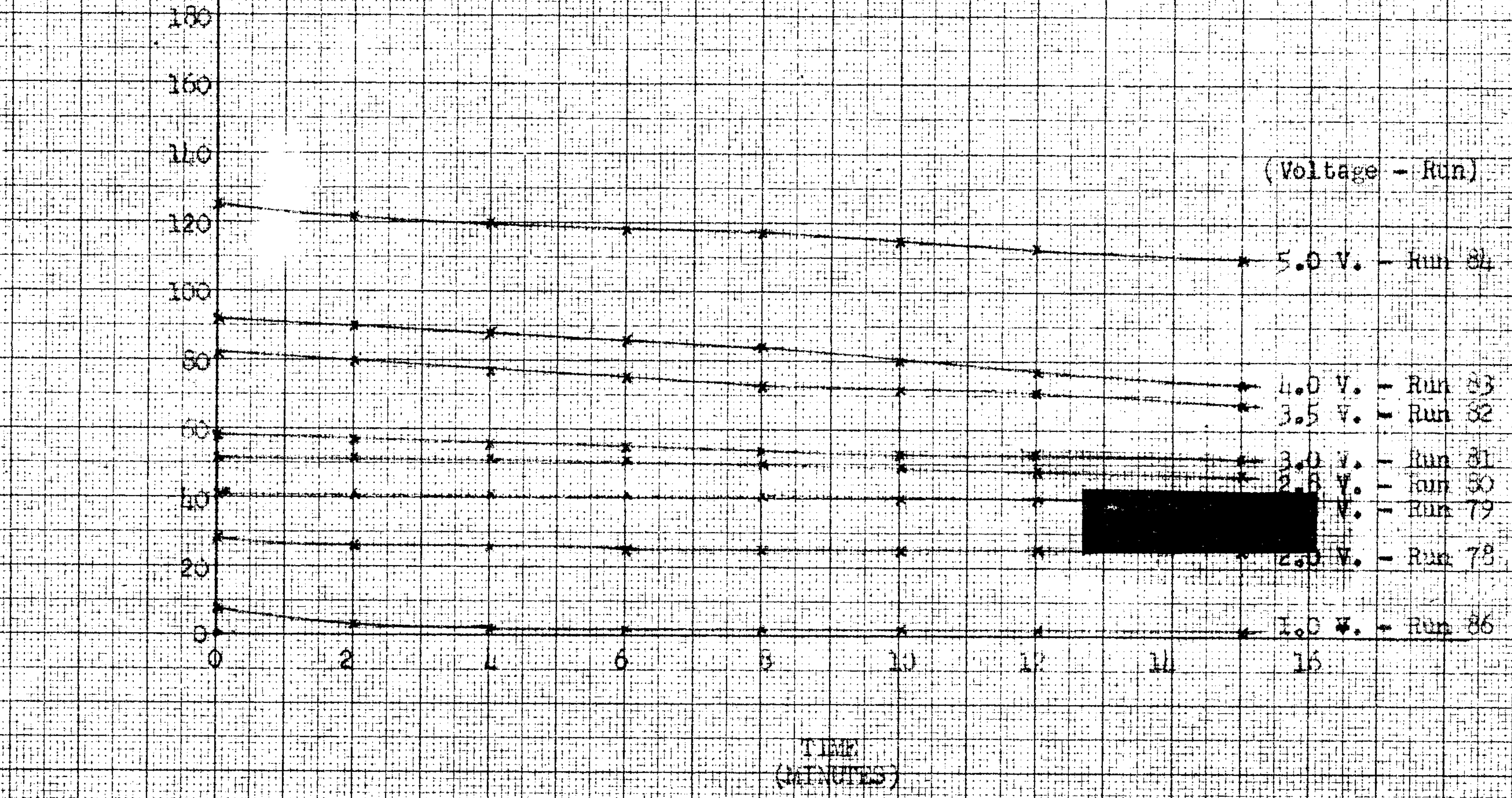
GRAPH 1. - TIME VS CURRENT FOR 1% MEDIUM VISCOSITY CMC.

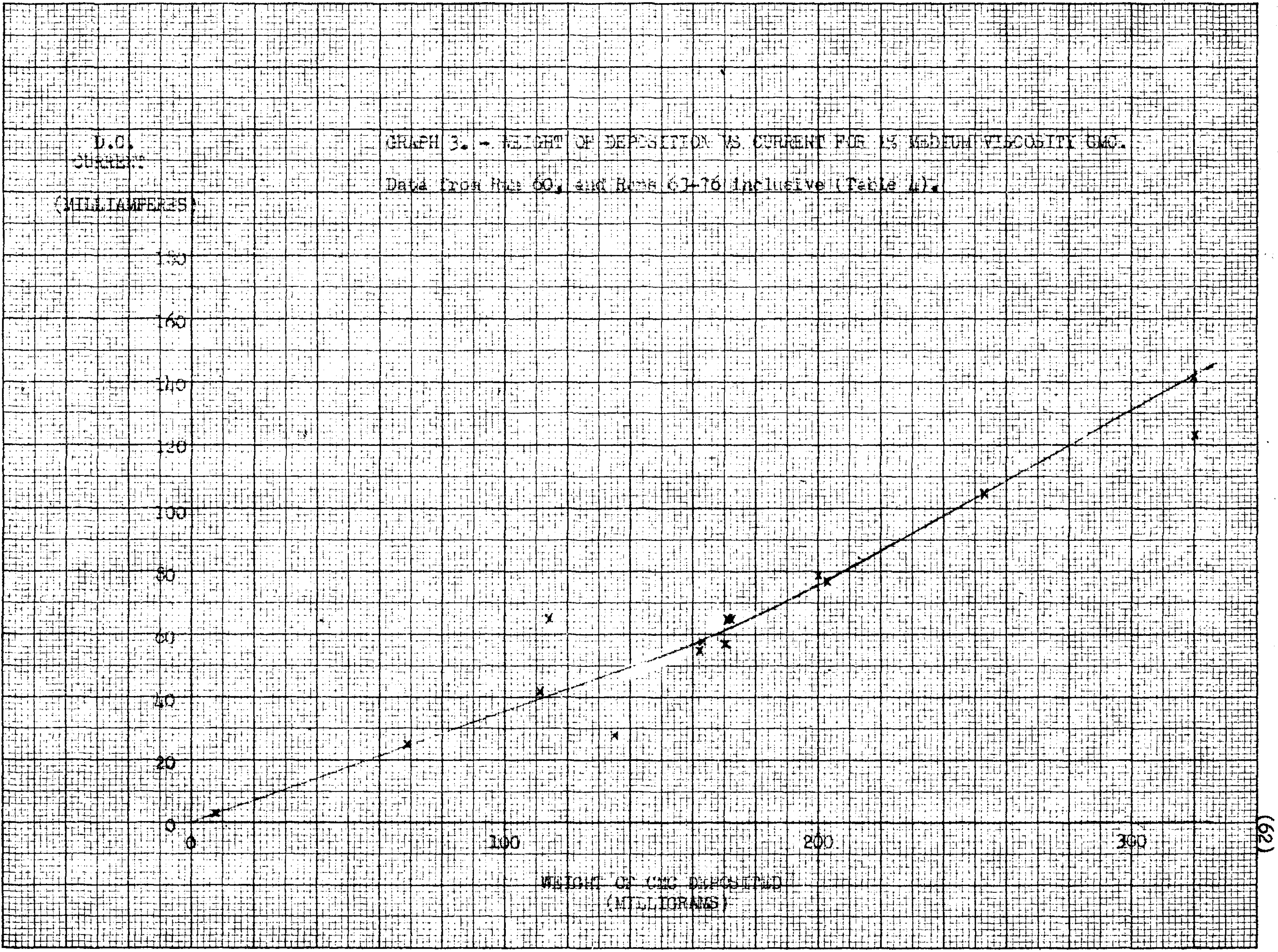
The relationship of current and time are shown for the series of plating runs made on Lot B, 1% medium viscosity CMC. Run 73 - made on Lot C - is shown for comparison. The voltage was held constant for all runs.



GRAPH 2. – TIME VS CURRENT FOR 1% HIGH VISCOSITY CMC.

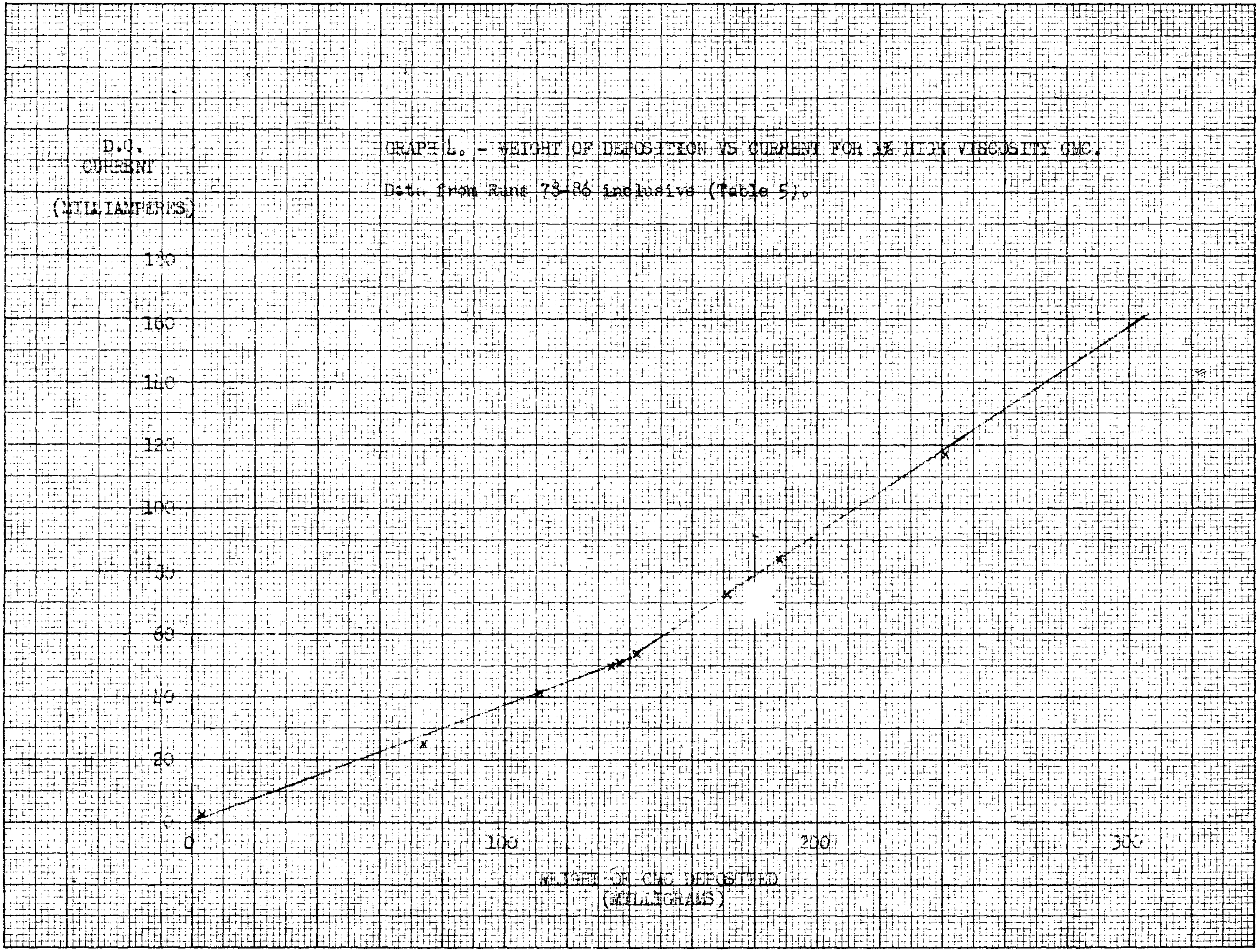
The relationship of current and time are shown for a series of plating runs, in which the voltage was held constant, for 1% high viscosity CMC.





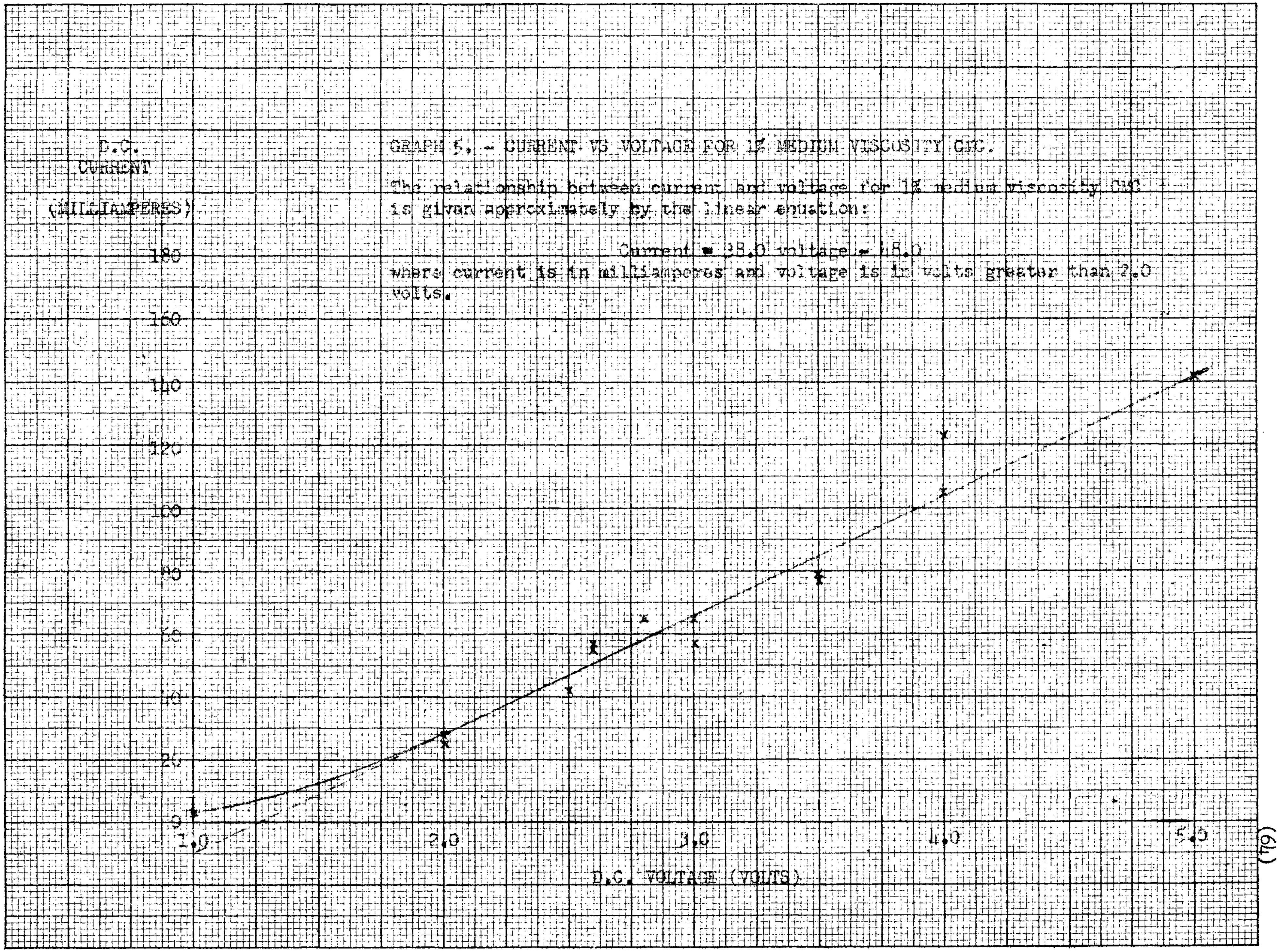
GRAPH 3. - WEIGHT OF DEPOSITION VS CURRENT FOR 1% MEDIUM VISCOSITY CMC.

Data from Run 60, and Runs 63-76 inclusive (Table 4).



GRAPH 4. - WEIGHT OF DEPOSITION VS CURRENT FOR 1% HIGH VISCOSITY CMC.

Data from Runs 73-86 inclusive (Table 5).

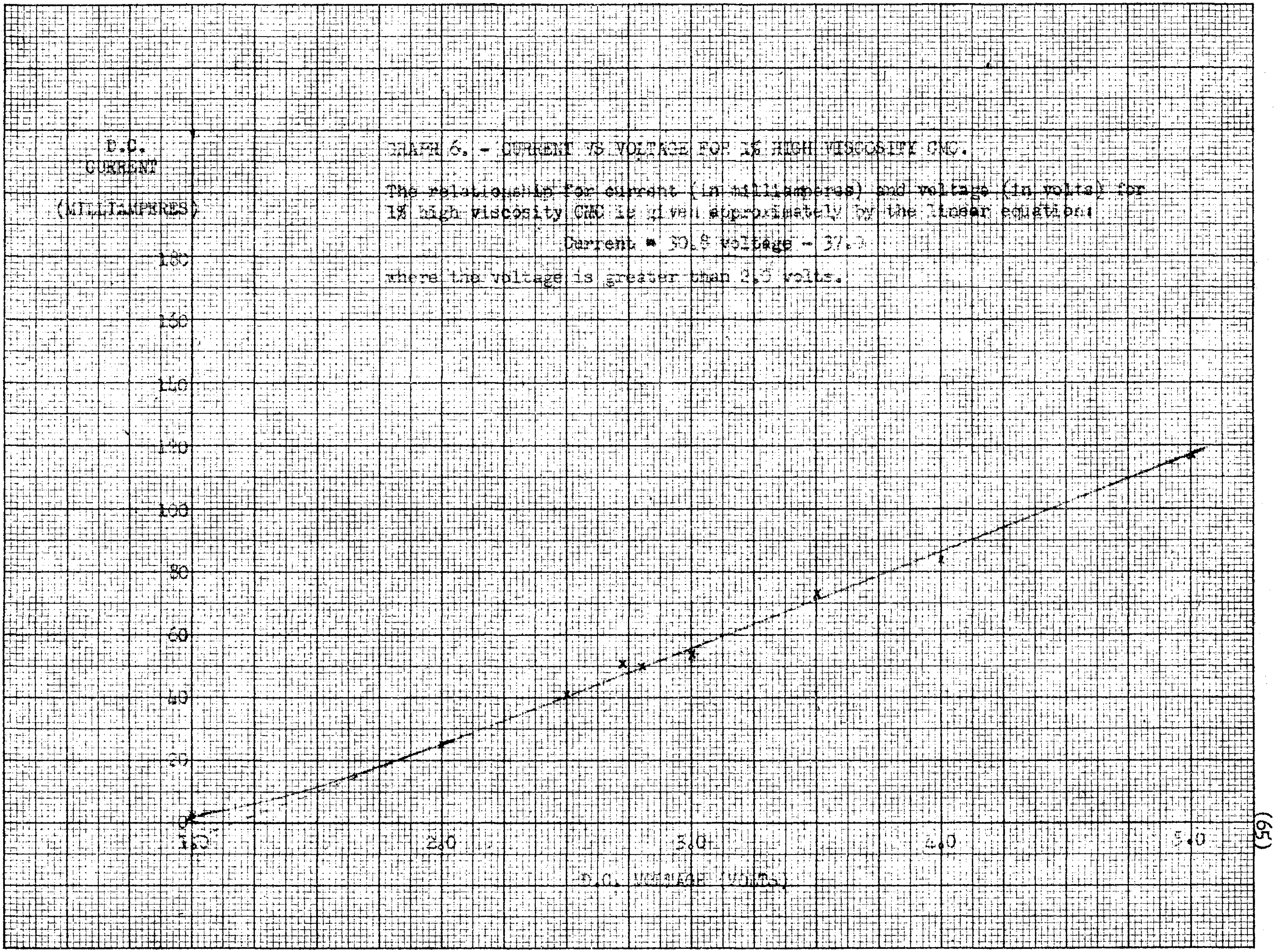


GRAPH 5. - CURRENT VS VOLTAGE FOR 1% MEDIUM VISCOSITY CMC.

The relationship between current and voltage for 1% medium viscosity CMC is given approximately by the linear equation:

Current = 38.0 voltage - 48.0

where current is in milliamperes and voltage is in volts greater than 2.0 volts.



GRAPH 6. - CURRENT VS VOLTAGE FOR 1% HIGH VISCOSITY CMC.

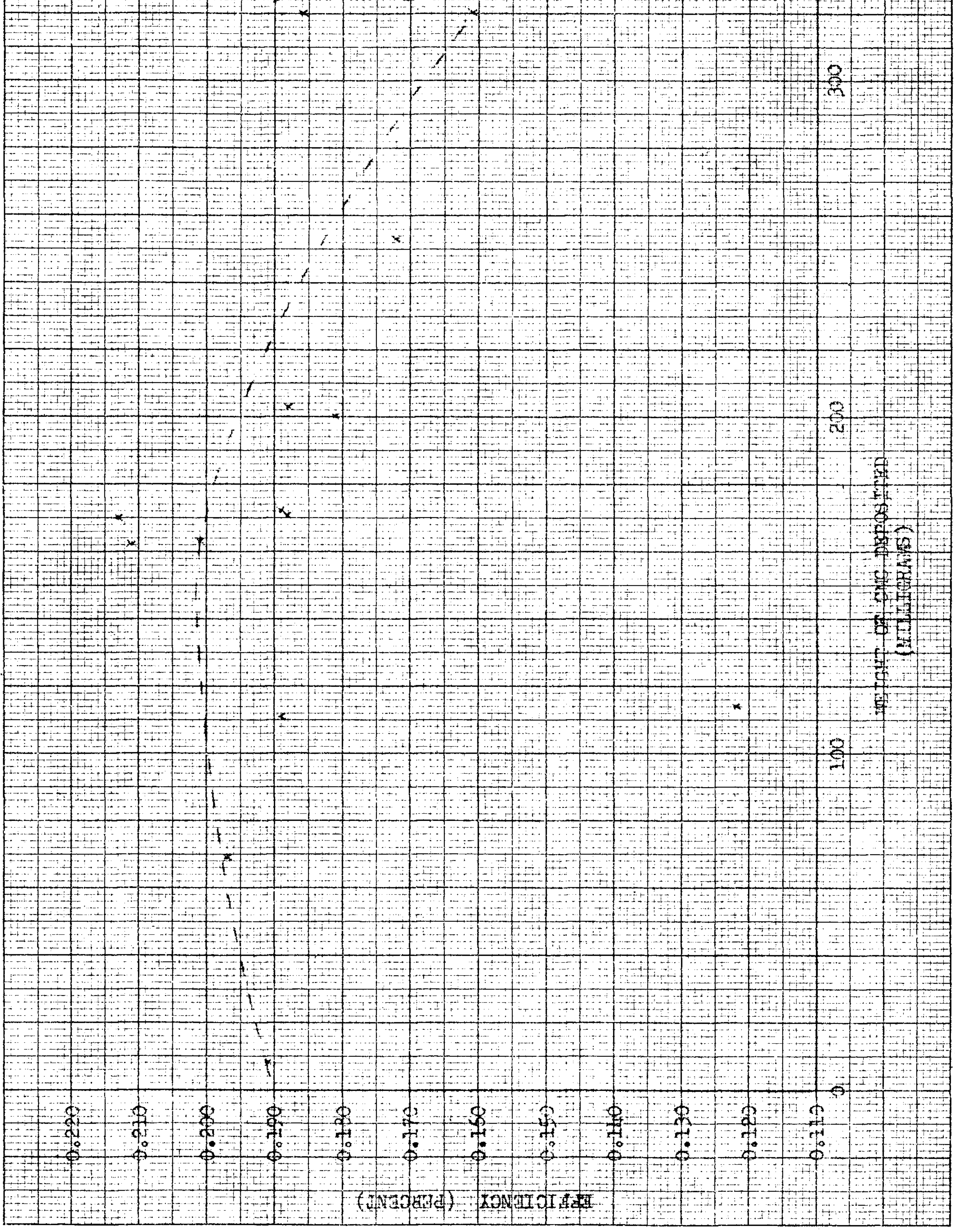
The relationship for current (in milliamperes) and voltage (in volts) for 1% high viscosity CMC is given approximately by the linear equation:

Current = 30.8 voltage - 37.3

where the voltage is greater than 2.5 volts.

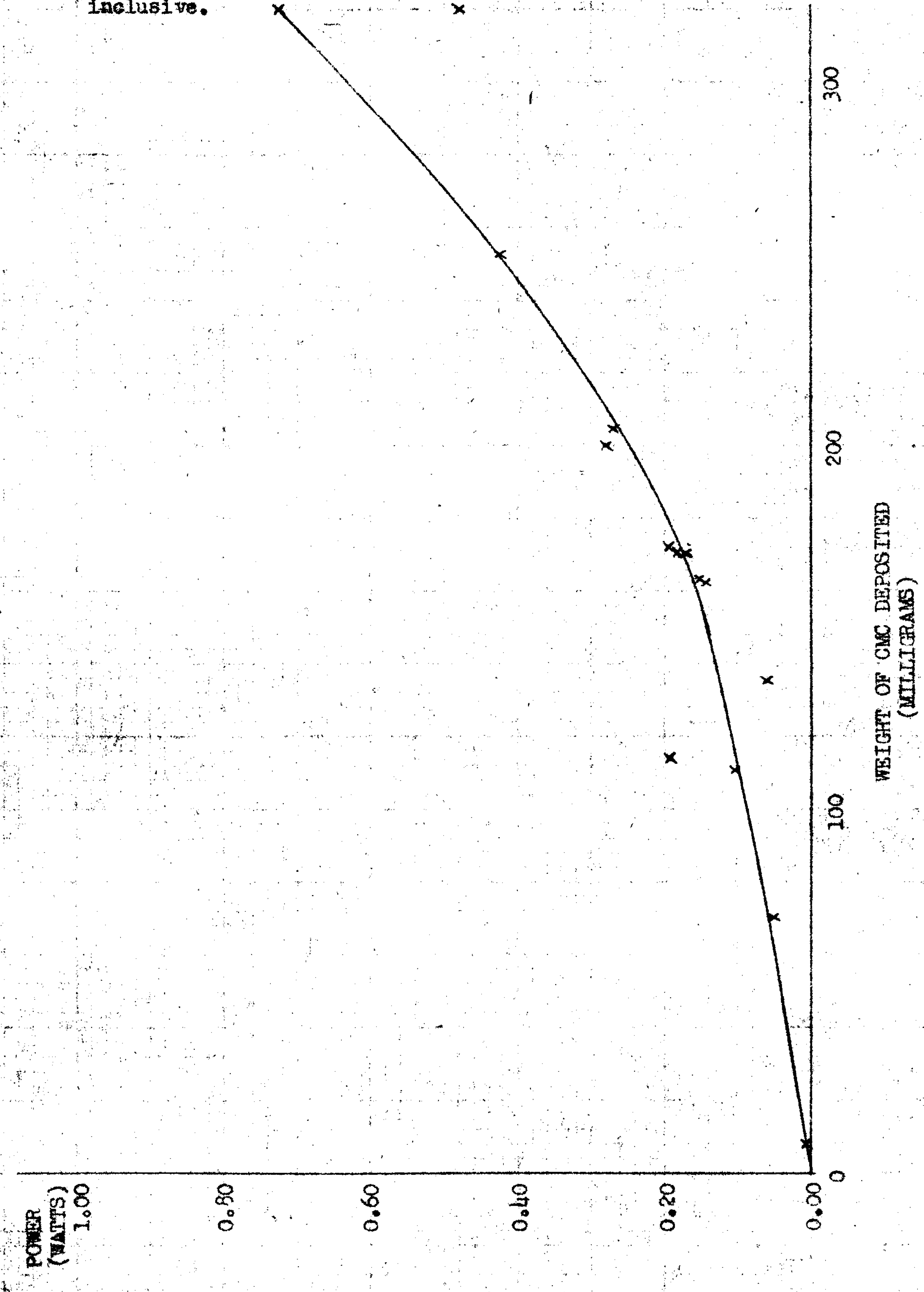
GRAPH 7. - EFFICIENCY OF CMC ELECTRODEPOSITION FOR 1% MEDIUM VISCOSITY CMC

A possible relationship between Efficiency and the weight of CMC deposited is shown for 1% medium viscosity CMC. Data from Run 60, and Runs 63-76 inclusive.



GRAPH 8. - POWER VS WEIGHT OF DEPOSITION FOR 1% MEDIUM VISCOSITY CMC

The relationship of power required versus the weight of CMC deposited is demonstrated. The power requirement herein is for the plating cell and bath. Data from Run 60, and Runs 63-76 inclusive.



APPENDIX D

The data for each individual run made on the electrodepositon of medium viscosity and high viscosity CMC are given. The runs start with Run 55, next Run 60, and thereafter are listed in consecutive order ending with Run 88.

DATA FOR RUN 55

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.225 Amperes/square foot

Time (Minutes)	Voltage (DC volts)	Current (DC milliamps)	Weight of CMC deposited:
0	3.00	22	0.085 grams
2	3.00	21	
4	3.00	20	
6	3.00	20	
8	3.00	20	
10	3.00	20	

Remarks: This was a trial run - to determine whether CMC deposited or not. A green colored deposit was found on the anode. Although there was an evolution of bubbles at the cathode, there was no loss in weight of the cathode at the end of the 10 minute plating trial. The microbubbles of gas evolved were so fine as to prohibit means of collecting them under the conditions of the experiment.

The anode deposit was rinsed with water, dipped in methanol for 1 minute, and air dried for 1 hour. The deposit was not friable, seemed to peel wasily from anode, and didnot crumble as the deposits obtained from sodium zincate-urea-cellulose solutions. Deposit seemed to possess strength and didnot break when a small section was pulled by the fingers.

DATA FOR RUN 60

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.635 amperes/square foot

Time (Minutes)	Voltage (DCVolts)	Current (DC Milliamps)
0	3.00	60
2	3.00	58
4	3.00	57
6	3.00	57
8	3.00	56
10	3.00	56
12	3.00	55
15	3.00	55

Weight of CMC deposited:
0.170 grams

Ash at 800°C:
14.90%

Remarks: Microbubbles of gas obtained at cathode and pale green deposit on anode. Deposit was water rinsed, methanol dipped, air dried and weighed. A little shrinkage occurs in the drying of the deposit (estimated at less than 10%). Deposit peeled easily from electrode.

Deposit is a face deposit with very little deposition on the back of the electrode except for edges.

DATA FOR RUN 61

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper cathode; brass screen anode; immersed to 3.2 inches, 1 inch apart

Current Density: 0.691 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	62
2	3.00	62
4	3.00	62
6	3.00	62
8	3.00	61
10	3.00	61
12	3.00	61
15	3.00	61

Weight of CMC deposited:

0.118 grams

Ash at 800°C:
(Not determined)

Remarks: In spite of the use of a brass screen, the deposit was again on the face side of the brass screen anode, with very little deposition on the back. Screen was water rinsed, methanol dipped, air dried, and weighed. After several weeks, the deposit was still adhering to the screen - no means for its removal were found. Microbubbles of gas were discharged at cathode.

DATA FOR RUN 62

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper cathode; Nickel anode; immersed to 3.3 inches, 1 inch apart

Current Density: 0.568 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	52
2	3.00	52
4	3.00	52
6	3.00	52
8	3.00	52
10	3.00	52
12	3.00	51
15	3.00	51

Weight of CMC deposited:
0.112 grams

Ash at 800°C:
2.96%

Remarks: Microbubbles at cathode. Anode deposit was water rinsed, methanol dipped, air dried, and weighed. However, deposit did not "DRY", but remained as a gelatinous semi-solid material. The deposit at anode edges appeared to be more like the solid film deposits obtained with copper electrodes. The differentiation in deposits poses interesting prospects. Deposit was water-white in color, rather than green.

DATA FOR RUN 63

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.731 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	67
2	3.00	67
4	3.00	66
6	3.00	65
8	3.00	65
10	3.00	65
12	3.00	65
15	3.00	64

Weight of CMC deposited:
0.111 grams

Ash at 800°C (after acid treatment):
0.46%

Remarks: Microbubbles at cathode. Pale green anode deposit was water rinsed, methanol dipped, air dried and weighed. A part of the anode deposit was treated for 1 minute by dipping in 20% hydrochloric acid - the acid made the deposit gummy, similar to the gelatinous semi-solid deposit obtained in the previous run. The ash was determined on the acid treated portion of deposit.

Another small piece of the original deposit was left in 20% HCl and dissolved in less than 5 minutes, while a similar piece placed in water did not dissolve even after several weeks standing and a third piece was insoluble in 10% NaOH. The resistance with the electrodes in the bath was found to be 400 ohms using the 4 M set and 4 K scale on the Triplett meter. Neut numbers were determined on a portion of the bath before and after plating run.

DATA FOR RUN 64

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.1 inches, 1 inch apart

Current Density: 1.43 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	4.00	132
2	4.00	126
4	4.00	123
6	4.00	123
8	4.00	123
10	4.00	122
12	4.00	121
15	4.00	119

Weight of CMC deposited:

0.320 grams

Ash at 800°C:

16.58%

Remarks: The anode deposit obtained was thicker than those of previous runs and a darker green in color. When anode was pulled from plating bath, it was noted that the deposit contained semi-curved lines, with the immersed mid-point of each edge of the electrode as a loci or focal point. The deposit was water rinsed, methanol dipped, air dried, and weighed . It was then redipped in the methanol as a means of dampening the deposit to make its removal a little easier. As the deposit hit the methanol, a slight crack was heard and the deposit immediately broke free of the electrode. As in previous runs, the deposit was a face deposit with very little on the back of the electrode. Microbubbles at cathode.

DATA FOR RUN 65

Bath: 700 ml of Lot A, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.314 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.00	30
2	2.00	29
4	2.00	28
6	2.00	28
8	2.00	28
10	2.00	27
12	2.00	27
15	2.00	26

Weight of CMC deposited:

0.135 grams

Ash at 800°C:
17.24%

Remarks: Anode deposit was very thin, but had a glossy finish instead of a dull as previously obtained. Deposit was methanol dipped (after rinsing with water), air dried, and weighed. Microbubbles were obtained at cathode.

DATA FOR RUN 66

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.034 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	1.00	5.0
2	1.00	3.5
4	1.00	3.2
6	1.00	3.1
8	1.00	3.0
10	1.00	3.0
12	1.00	2.7
15	1.00	2.3

Weight of CMC deposited:

0.008 grams

Ash at 800°C:
(Not determined)

Remarks: Very little anode deposit, but semi-solid and gelatinous in nature. No microbubbles at cathode noted.

DATA FOR RUN 67

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.286 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.00	28.0
2	2.00	27.0
4	2.00	26.0
6	2.00	25.5
8	2.00	25.3
10	2.00	25.1
12	2.00	25.0
15	2.00	25.0

Weight of CMC deposited:

0.069 grams

Ash at 800°C:
16.12%

Remarks: Anode deposit water rinsed, methanol, air dried and weighed. Microbubbles at cathode.

DATA FOR RUN 68

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.472 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.50	43
2	2.50	42
4	2.50	42
6	2.50	42
8	2.50	42
10	2.50	42
12	2.50	42
15	2.50	42

Weight of CMC deposited:
0.111 Grams

Ash at 800°C:
13.32%

Remarks: Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit had a less glossy appearance than deposit from Run 67. Microbubbles at cathode.

DATA FOR RUN 69

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current density: 0.731 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	68
2	3.00	66
4	3.00	65
6	3.00	65
8	3.00	65
10	3.00	65
12	3.00	64
15	3.00	63

Weight of CMC deposited:

0.172 grams

Ash at 800°C:

14.60%

Remarks: Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit has a dull finish, and possesses slight parallel striation lines, running from top to bottom of deposit and parallel to the electrode edges. Microbubbles at cathode(microbubbles are so small and the quantity so minute, so as to make their collection and analysis almost impossible under the conditions of these experiments).

DATA FOR RUN 70

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.870 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.50	82
2	3.50	81
4	3.50	80
6	3.50	78
8	3.50	77
10	3.50	76
12	3.50	76
15	3.50	74

Weight of CMC deposited:
0.203 grams

Ash at 800°C:
13.90%

Remarks: Deposit was water rinsed, methanol dipped, air dried, and weighed. Parallel striation lines, running from top to bottom of deposit and parallel to the edges of the electrode, were noted - these were more intense than in the previous run and appeared to be more numerous. Microbubbles at cathode.

DATA FOR RUN 71

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart.

Current Density: 1.19 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	4.00	112
2	4.00	108
4	4.00	107
6	4.00	106
8	4.00	105
10	4.00	103
12	4.00	100
15	4.00	97

Weight of CMC deposited:

0.253 Grams

Ash at 800°C:

13.20%

Remarks: Deposit was water rinsed, methanol dipped, air dried, and weighed. Striation lines in deposit were semi-curved with each edge of the electrode acting as a loci or focal point. More intense and more numerous lines than in previous run. Microbubbles at cathode.

DATA FOR RUN 72

Bath: 700 ml of Lot B, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 1.61 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	5.00	170
2	5.00	160
4	5.00	150
6	5.00	145
8	5.00	142
10	5.00	140
12	5.00	137
15	5.00	135

Weight of CMC deposited:

0.320 grams

Ash at 800°C:
14.02%

Remarks: Very thick deposit, full of semi-curved striation lines, again with the electrode edges as focal points. Deposit was water rinsed, methanol dipped, air dried, and weighed. Microbubbles at cathode.

DATA FOR RUN 73

Bath: 700 ml of Lot C, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.1 inches, 1 inch apart

Current Density: 0.618 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.60	55
2	2.60	55
4	2.60	55
6	2.60	55
8	2.60	54
10	2.60	53
12	2.60	53
15	2.60	53

Weight of CMC deposited:

0.162 grams

Ash at 800°C:

15.91%

Remarks: Deposit was water rinsed, methanol dipped, air dried, and weighed. Very slight parallel striation lines were noted upon very close examination of the dried deposit. Microbubbles at cathode.

DATA FOR RUN 74

Bath: 700 ml of Lot C, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.646 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	2.60	60	0.163 grams
2	2.60	59	
4	2.60	58	
6	2.60	58	
8	2.60	57	
10	2.60	57	
12	2.60	57	
15	2.60	57	

Remarks: As noted in previous run, there were very slight parallel striation lines in dried deposit. Deposit was water rinsed, methanol dipped, air dried, and weighed.

Microbubbles at cathode.

DATA FOR RUN 75

Bath: 700 ml of Lot C, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.731 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.80	66
2	2.80	66
4	2.80	65
6	2.80	65
8	2.80	64
10	2.80	64
12	2.80	64
15	2.80	63

Weight of CMC deposited:

0.171 grams

Ash at 800°C:
15.41%

Remarks: Slight parallel striation lines were noted in dried anode deposit, and were but little more pronounced than in previous two runs. Deposit was water rinsed, methanol dipped, air dried, and weighed. Microbubbles at cathode.

DATA FOR RUN 76

Bath: 700 ml of Lot C, 1% medium viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.89 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.50	82
2	3.50	80
4	3.50	79
6	3.50	79
8	3.50	79
10	3.50	78
12	3.50	78
15	3.50	77

Weight of CMC deposited:

0.200 grams

Ash at 800°C:
17.00%

Remarks: Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Parallel striation lines are definitely apparent in all deposits with a voltage of 3.0 and over. Microbubbles at cathode.

DATA FOR RUN 77

Bath: 700 ml of Lot C, 1% medium viscosity CMC

Electrodes: Nickel anode and nickel cathode, immersed to 3.3 inches, 1 inch apart

Current Density: 1.05 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.50	97
2	3.50	97
4	3.50	97
6	3.50	96
8	3.50	96
10	3.50	96
12	3.50	96
15	3.50	96

Weight of CMC deposited:
0.185 grams

Ash at 800°C:
11.62%

Remarks: Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit, in contrast to that obtained in Run 62 (Cu^-,Ni^+), "dried", but rather than being a smooth, solid deposit, is one which is filled with small holes of varying sizes, giving a lacework or crystalline latticework appearance. It appears to be not quite as flexible as the deposits produced on copper electrode pairs, although was readily removed from the anode. Like the copper pair deposits, the deposit was a face deposit; that produced on the edges and back seemed partially gummy. Microbubbles were produced at the cathode.

DATA FOR RUN 78

Bath: 700 ml of LotD, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches,1 inch apart

Current Density: 0.281 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	2.00	28	0.074 grams
2	2.00	26	
4	2.00	26	
6	2.00	25	
8	2.00	25	
10	2.00	25	
12	2.00	25	
15	2.00	24	

Remarks: Microbubbles at cathode. Deposit on anode, rinsed with water after run, dipped in methanol, air dried and weighed. Smooth deposit, glossy in nature, but rather thin and seemingly frail although removed from anode without difficulty.

DATA FOR RUN 79

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.461 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	2.50	41	0.111 grams
2	2.50	41	
4	2.50	41	
6	2.50	41	
8	2.50	41	
10	2.50	40	
12	2.50	40	
15	2.50	39	

Remarks: Microbubbles at cathode. Deposit water rinsed, methanol dipped, air dried, and weighed. Deposit was less glossy than previous run, and heavier in thickness.

DATA FOR RUN 80

Bath: 700 ml of Lot D, 1% high viscosityCMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches,1 inch apart

Current Density: 0.570 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	2.80	52	0.134 grams
2	2.80	52	
4	2.80	52	
6	2.80	51	
8	2.80	50	
10	2.80	49	
12	2.80	48	
15	2.80	47	

Remarks: Microbubbles at cathode. Anode deposit was water rinsed, methanol dipped, air dried and weighed. Deposit had a dull finish, smooth characteristics.

DATA FOR RUN 81

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.618 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	58
2	3.00	57
4	3.00	56
6	3.00	55
8	3.00	54
10	3.00	53
12	3.00	53
15	3.00	52

Weight of CMC deposited:

0.142 grams

Remarks: Microbubbles at cathode. Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit had a dull finish, and contained parallel striation lines, as noted in the deposits previously obtained for medium viscosity CMC at 3.0 volts.

DATA FOR RUN 82

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.84 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	3.50	82	0.171 grams
2	3.50	80	
4	3.50	77	
6	3.50	75	
8	3.50	73	
10	3.50	72	
12	3.50	71	
15	3.50	68	

Remarks: Microbubbles at cathode. Anode deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit had a dull finish and contained parallel striation lines. Face deposit with but little deposit on back of anode.

DATA FOR RUN 83

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.96 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	4.00	92	0.188 grams
2	4.00	90	
4	4.00	88	
6	4.00	86	
8	4.00	84	
10	4.00	80	
12	4.00	77	
15	4.00	74	

Remarks: Microbubbles at cathode. Deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit contained semi-curved striation lines, with the immersion mid-point of each edge of the anode acting as a focal point. Like previous deposits was a face deposit, with very little deposition on the back of anode except for along back edges. Deposit was much thicker than previous, dull in appearance.

DATA FOR RUN 84

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 1.32 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	5.00	125	0.241 grams
2	5.00	122	
4	5.00	120	
6	5.00	118	
8	5.00	117	
10	5.00	115	
12	5.00	113	
15	5.00	110	

Remarks: Microbubbles at cathode. Deposit was water rinsed, methanol dipped, air dried, and weighed. Deposit contained semi-curved striation lines, with the immersion mid-point of each edge of the anode acting as a loci or focal point. Deposit(as previous) was green in color, dull appearance, and very thick - almost leathery in character, and so filled with striation marks as to give it a "crackled" effect. Face deposit, very little deposition on back of anode, except for edges.

DATA FOR RUN 85

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.57 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	2.72	54
2	2.72	52
4	2.72	51
6	2.72	51
8	2.72	51
10	2.72	50
12	2.72	49
15	2.72	48

Weight of CMC deposited:

0.138 grams

Ash at 800°C:

15.21%

Remarks: Microbubbles at cathode. Anode deposit was water rinsed, methanol dipped, air dried, and weighed.

Oxygen analysis of hi vis CMC: 41.70%

Oxygen analysis of deposit: 42.16%

Ferrous sulfate test for oxygen in cathodic microbubbles was negative indicating absence of oxygen. The microbubbles were collected with a porcelain spatula, placed in a small vial, about 50 mgs. of ferrous sulfate added, and shaken.

Solubility was determined on 10-11 samples of the deposit.

DATA FOR RUN 86

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Copper anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.028 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited
0	1.00	8.0	0.003 grams
2	1.00	3.0	
4	1.00	2.5	
6	1.00	2.4	
8	1.00	2.4	
10	1.00	2.3	
12	1.00	2.3	
15	1.00	2.3	

Remarks: Microbubbles at cathode. Deposit consisted of small specks scattered over anode face, was water rinsed, methanol dipped, air dried and weighed.

DATA FOR RUN 87

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Nickel anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.54 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)	Weight of CMC deposited:
0	2.70	48	0.113 grams
2	2.70	48	
4	2.70	48	Ash at 800°C: 10.59%
6	2.70	48	
8	2.70	48	
10	2.70	48	
12	2.70	48	
15	2.70	48	

Remarks: Microbubbles at cathode. Deposit was gummy. Deposit was water rinsed, methanol dipped, air dried, and weighed. Minute bubbles in deposit, deposition seemed to occur around the bubbles.

DATA FOR RUN 88

Bath: 700 ml of Lot D, 1% high viscosity CMC

Electrodes: Nickel anode and cathode, immersed to 3.2 inches, 1 inch apart

Current Density: 0.62 amperes/square foot

Time (Minutes)	Voltage (DC Volts)	Current (DC Milliamps)
0	3.00	54
2	3.00	55
4	3.00	55
6	3.00	55
8	3.00	55
10	3.00	55
12	3.00	55
15	3.00	55

Weight of CMC deposited:

0.144 grams

Ash at 800°C:

11.68%

Remarks: Microbubbles at cathode. Deposit was slightly gummy, semi-solid, contained minute bubbles. Deposit was water rinsed, methanol dipped, air dried and weighed.

Deposition occurred around the minute bubbles.