CHAPTER 4

EXPERIMENTAL DESIGNS FOR COPPER ELECTROWINNING

4.1. Introduction

It has been shown that polyacrylamide prepared in 16-fold diluted electrolyte at 50^{o}C for 2-hours under stirring has a statistically significantly lower mean surface roughness than either polyacrylamide prepared in water or in full-strength electrolyte. It also produced lower surface roughness than polyacrylic acid. This result may be interpreted to mean that this method of preparation results in a higher surface coverage of the copper metal and stainless steel substrates than the preparation media in water and full-strength electrolyte. It is widely recognised in the literature that surface coverage of an organic additive in metals electrodeposition and corrosion is directly related to its adsorption onto the substrate[1, 2].

In the work described in this Chapter, the following studies were conducted to evaluate Guar and APAM. The electrowinning time was the most important variable to follow on the evaluation of both additives.

(i) Two fractional factorial experimental designs were devised to evaluate whether Guar, the industry-standard additive for copper electrowinning, or APAM act independently or perform the same role as levelling agent.

(ii) The role of Guar and APAM was studied using an extended ratio of Guar to APAM concentrations in a 2^2 experimental design to determine whether an optimum concentration ratio exists to effectively reduce surface roughness.

(iii) Guar and APAM were directly compared in a Guar or APAM 2^2 experimental design to evaluate their effectiveness on the surface roughness of the copper deposit at 4.64, 6 and 12 Hours EW time.

The variables in commercial copper electrowinning and electrorefining are the flow rate of the feed electrolyte into the electrolytic cells, electrolyte temperature, current density, and copper, sulphuric acid, chloride ions and fresh organic additive(s) concentrations. An increment of the electrolyte flow rate into the electrolytic cell also increases the velocity of the bulk electrolyte closest to the cathode and therefore may also decrease the value of the diffusion layer thickness. The experimental designs selected for this work use high and low levels of these variables, including Guar and APAM to closely replicate the industry-standard operating conditions of commercial copper electrowinning. Fractional factorial experimental designs are a variation of a basic factorial design in which only a subset of the runs are made to minimize the number of experiments but include all the process variables[3].

The two fractional factorial experimental designs have low and high temperature levels of 45^{o}C and 55^{o}C and, 45^{o}C and 64^{o}C to evaluate APAM at electrolyte temperatures similar to commercial copper electrowinning and electrorefining conditions.

4.2 Experimental Conditions

Table 4-12 shows the electrolyte conditions and the preparation media for polyacrylamide described in Section 3.3. APAM was prepared in 16-fold diluted electrolyte at 50^{o}C for 2 hours under stirring conditions. The evaluation of Guar and APAM was carried out using the rotating cylinder electrode described also in Section 2.3.

The Guar concentration used at Mt. Gordon was approximately 0.52mg/L electrolyte at the new tankhouse or 175 grams Guar/tonne copper cathode. This concentration was used as the low level factor in the experimental design and the high level was set at 1mg/L electrolyte. Guar was prepared in water at room temperature as per commercial operation and under similar stirring conditions described for APAM. Guar was dosed *twice* throughout the testwork. The first dose was added at the beginning and the second at one at approximately half EW time (2hours 10minutes or 2hours 21minutes) depending on the current density. The total electrowinning time was 4hrs 21 minutes at a current density of 320A/m^2 and 4hrs 58 minutes at 280A/m^2.

Table 4-12: Electrolyte Composition and Additives Preparation Media

Copper, g/L	36
Sulphuric Acid, g/L	160
Chloride Ions, mg/L	25
PAM Preparation Media – 16 fold Diluted Electrolyte, Temp. ^oC	50
Guar Preparation Media, water, Temperature, ^oC	25
Number of Coulombs per cm^2	500

The organic additives, once dosed to the electrolyte, were subjected to 15 minutes mixing at 40 rpm and 5 minutes at the rpm value to be evaluated (10, 17.5 or 25) before the application of the desired current to the electrolytic cell. Therefore the total residence time of the organic additives in the electrolyte was *20 minutes* in addition to the electrowinning times at 45^{o}C, 50^{o}C or 65^{o}C ± 0.5^{o}C. APAM was dosed *once* during this testwork. Figure 4-24 shows the rotating cylinder electrode in operation.

The surface roughness was collected using a Mahr Perthometer M1[4] with a 2μm stylus tip radius. A detailed description about this measurement was given in Section 3.2.1. The surface roughness evaluation includes analysis of variance (ANOVA) and statistical inference procedures using Design-Expert® software (Stat-Ease, Version 6.0.10, 2003)[5]. The adequacy of the models was checked using residual analysis as described by Montgomery[3].

The cross-section of the copper deposits was prepared for Scanning Electron Microscopy (SEM). The samples were embedded in an epoxy resin and the cross-

section cut with 600 grit silicon carbide powder on a round table. It was then sequentially polished with 3, 1 and 0.25µm diamond paste from Struers. It was finally etched with a solution of 5 g of ferric chloride and 5mL hydrochloric acid in 90mL ethanol for 20-25 seconds.

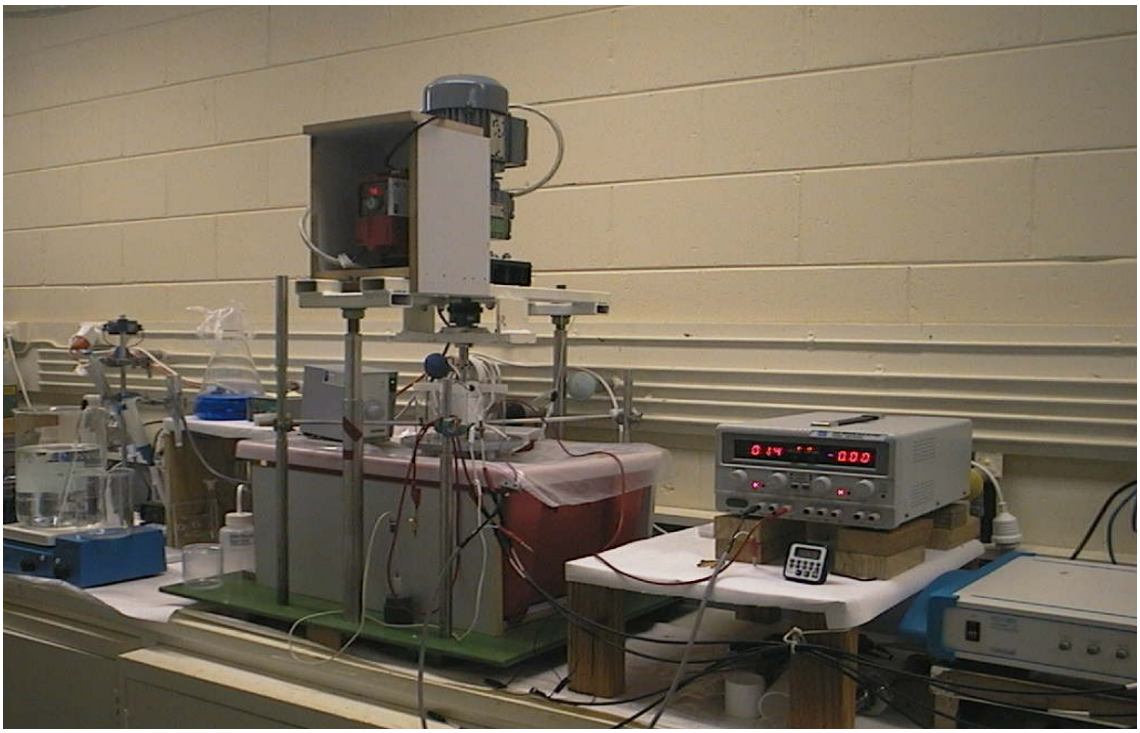

Figure 4-24: Rotating Cylinder Electrode Equipment

4.2.1 Copper Electrowinning and the Effect of its Main Operating Variables

Table 4-13 shows the two 2^{5-2} fractional factorial experimental designs. The factors at low level are common for both designs. The factors at high level differ in temperature only. The values of the limiting current density and diffusion layer thickness were derived using the equation developed by Arvia et al.[6] and Fick[7], respectively, using Mathcad 12[8] as described in Chapter 3 – Section 3.2.3. It should be noted that variations in temperature affect the diffusion layer thickness are linked through the Schmidt number (ν/D).

Table 4-13: Two 2^{5-2} Fractional Factorial Experimental Designs

Factors		Factor Level		
		Low	High	
A	T (Temperature, ^{o}C)	45	55	65
B	i (Current Density, A.m^{-2})	280	320	320
C	L (Guar, mg/L)	0.5	1	1
D	S (APAM, mg/L)	0.5	1	1
E	δ (Diffusion Layer Thickness, μm)	87 (25rpm)	108 (10rpm)	110 (10rpm)

4.3 Experimental Results

4.3.1 2^{5-2} Experimental Design Results at 45^{o}C - 55^{o}C

Table 4-14 presents the results indicating the effect of temperature (A), current density (B), Guar concentration (C), APAM concentration (D) and diffusion layer thickness (E) on surface roughness.

The regression model obtained from this testwork is shown in Equation 4-19. An F-value of 9.41 implies that the model is significant. There is only a 0.01% chance that the model F-value this large could occur due to noise. If the "Prob > F value" (α) is very small (less than 0.05), then the terms in the model have a significant effect on the response[3, 5].

Surface Roughness (μm) =

$$+6.26+0.27*B-0.053*C-0.056*D+0.25*E-0.62*B*C-0.38*B*E \quad (4\text{-}19)$$

It can be seen that the surface roughness is strongly influenced by an increment of the current density B, (α=0.0180) and diffusion layer thickness E, (α=0.0247). In addition, it is evident that there are two strong interacting terms involving B*C (Current Density*Guar, α<0.0001) and B*E (Current Density*Diffusion Layer Thickness, α=0.0009) which decreases the surface roughness. APAM (D, α=0.6098) and Guar (C, α=0.6316) have an insignificant effect on reducing surface roughness in this temperature range. The regression analysis also indicates that APAM and Guar are not

aliased -that is no C*D term appears in Equation 4-19, APAM appears to act independent of Guar[3].

Figure 4-25 shows the effect of the aliased and significant variables Current Density and Diffusion Layer Thickness on surface roughness. It clearly indicates that at high rotational speed of the cylinder and low current density the smoothest surface roughness is achieved.

Table 4-14: 2^{5-2} Fractional Factorial Experimental Results–Temperature Levels 45°C-55°C

	A	B	C	D=A*B#	E=A*C#	Mean Surface	Std.
Run	Temp.,	C.Density	Guar	APAM	DLayerT	Roughness	Dev.
Std	°C	mA/cm^2	mg/L	mg/L	µm	Ra, µm	
1	45	28	0.50	1.00	108	5.95	0.47
2	55	28	0.50	0.50	87	4.90	0.42
3	45	32	0.50	0.50	108	7.08	1.38
4	55	32	0.50	1.00	87	7.33	1.09
5	45	28	1.00	1.00	87	5.83	0.72
6	55	28	1.00	0.50	108	7.31	1.08
7	45	32	1.00	0.50	87	5.99	0.66
8	55	32	1.00	1.00	108	5.71	0.68
CP	50	30	0.75	0.75	97.50	7.04	0.93

#Level of factors D and E were determined by the levels of A*B and A*C, respectively.

Figure 4-26 shows the effect of the aliased and significant variables Current Density and Guar on surface roughness. It can be seen that increasing Guar concentration *increases* surface roughness at lower current densities than about 300A/m^2, a surprising result for an organic additive dosed to control dendrite formation. Moreover, it indicates that the surface roughness increases more steeply with an increment of the current density than with the increment of Guar concentration.

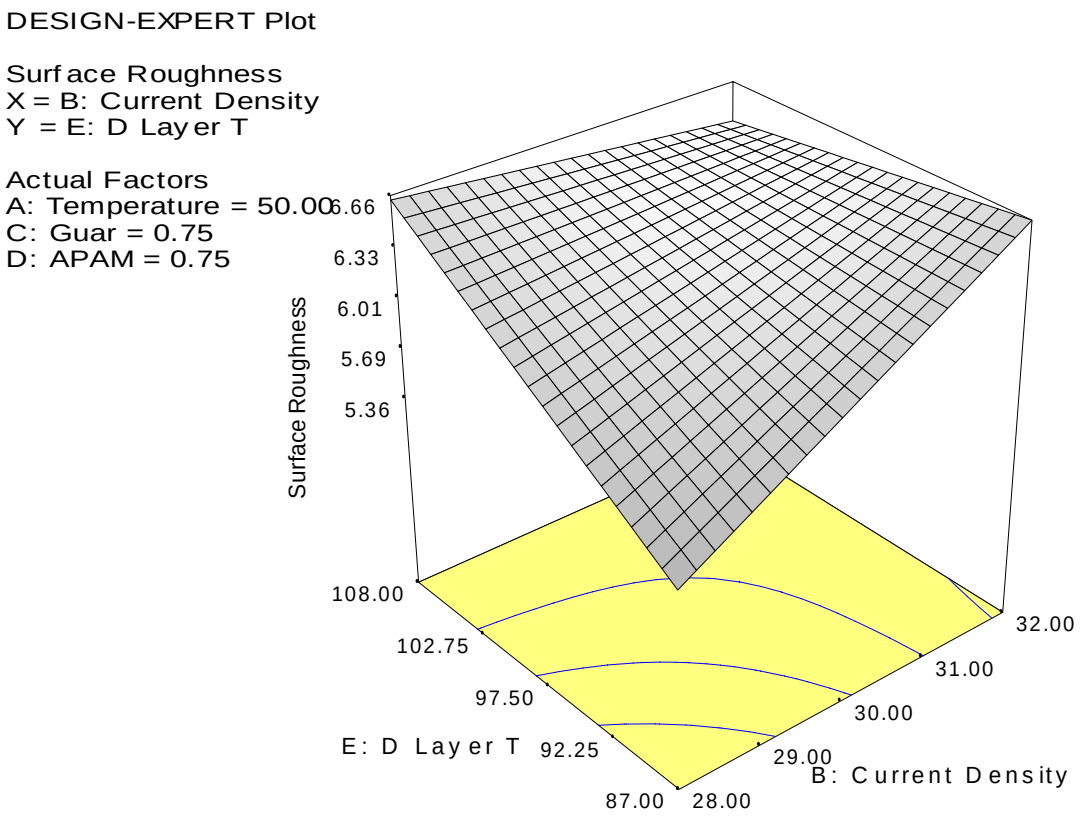

Figure 4-25: Effect of Diffusion Layer Thickness and Current Density on Surface Roughness

A: Temperature, ^{o}C; B: Current Density, mA/cm^2; C: Guar, mg/L; D: APAM, mg/L; E: D Layer Thickness, µm and Surface Roughness, µm

The adequacy of the model was tested graphically as shown in Figures 4-27, 4-28 and 4-29. An adequate model should show an almost straight line around the central values of the plot in Fig. 4-27, should show virtually all points in Figs. 4-28 and 4-29 within ± 3, and Fig. 4-29 should show a random distribution of the residual points[3, 5]. Based on these Figures, it is concluded that the model was adequate.

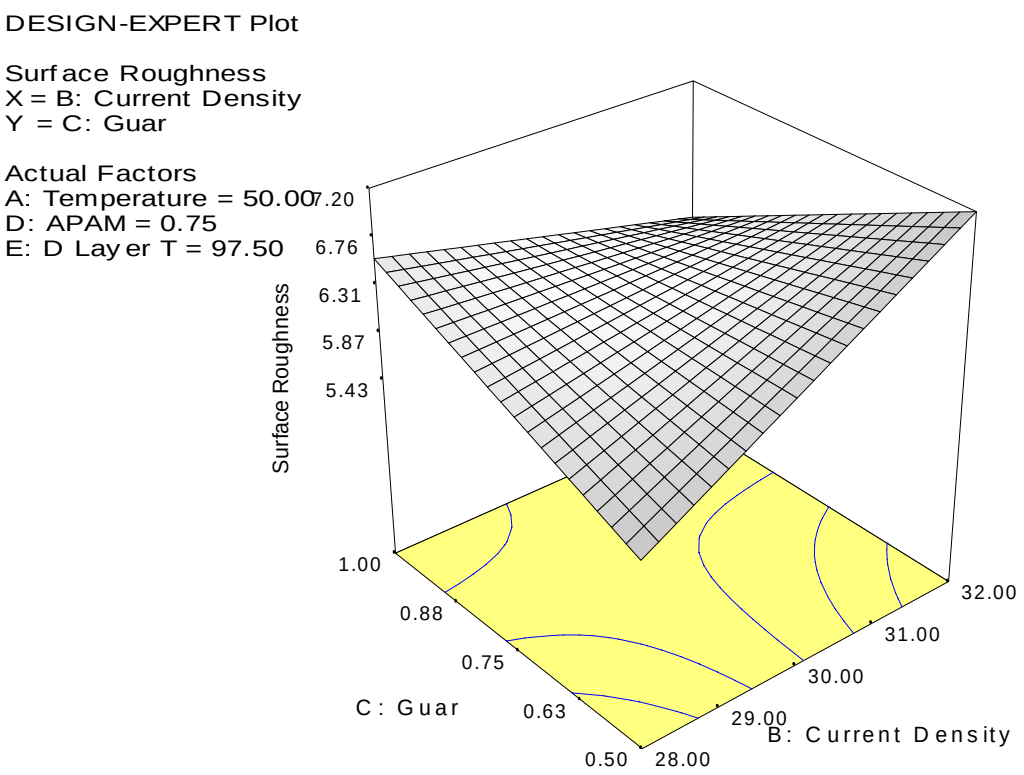

Figure 4-26: Effect of Current Density and Guar on Surface Roughness

A: Temperature, ^{o}C; B: Current Density, mA/cm^2; C: Guar, mg/L; D: APAM, mg/L; E: D Layer Thickness, µm and Surface Roughness, µm

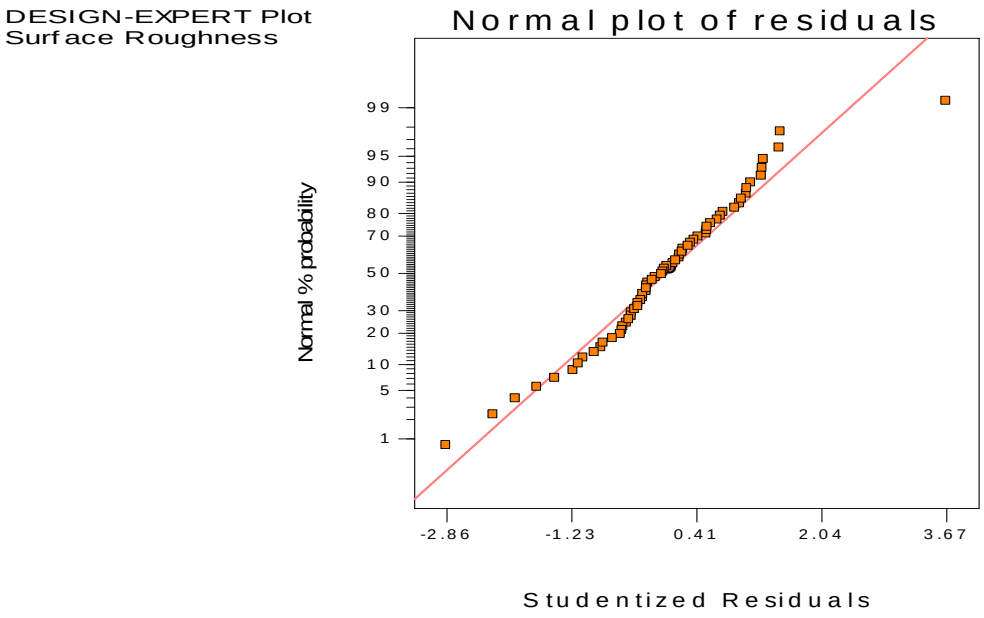

Figure 4- 27: Studentized Residuals Plot

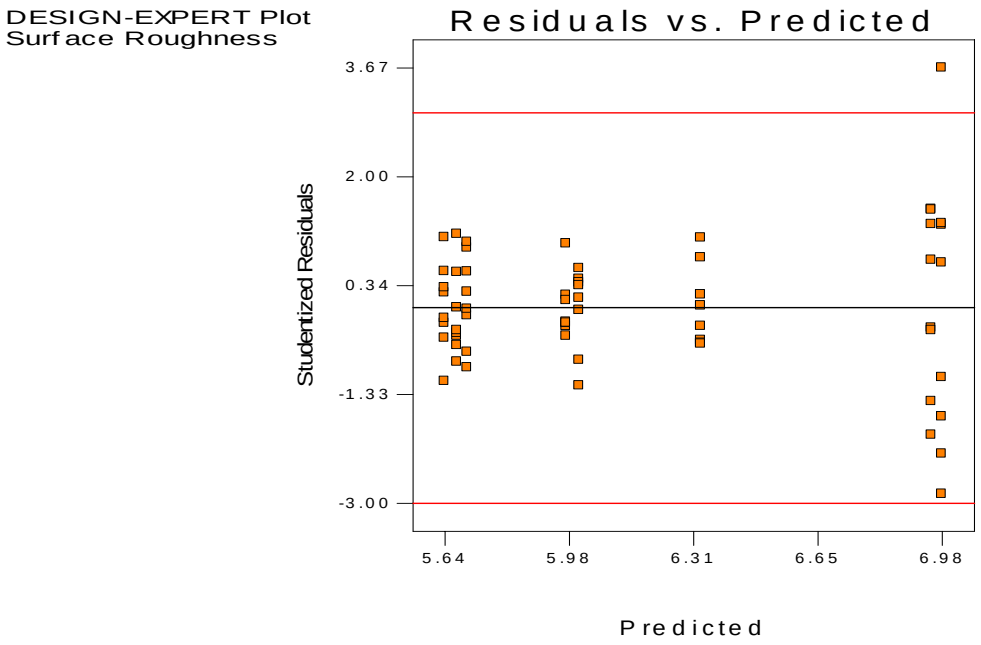

Figure 4-28: Residuals vs. Predicted Plot

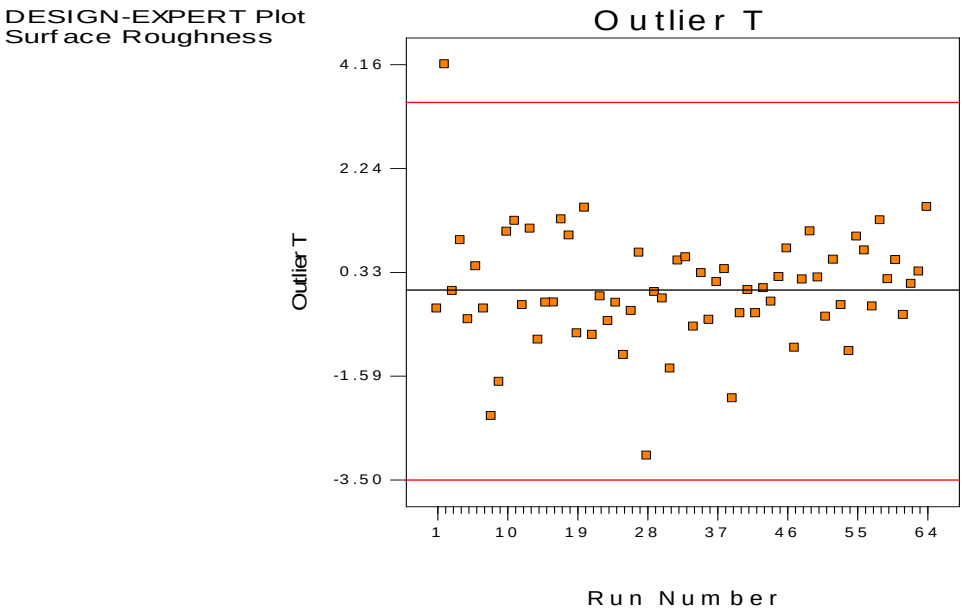

Figure 4-29: Outlier T Diagnostic Plot

The effect of APAM was insignificant in this temperature range possibly due to the kinetics of its ageing in the electrolyte. The rationale for this conclusion is as

follows. Cyclic Voltammetry tests indicate (Chapter 5 – Sections 5.4 and 5.5) that at 45°C, a maximum polarization of APAM was obtained at about 3 hours residence time in the electrolyte and at 65°C it was obtained at about 1hour residence time. EIS tests (Sections 5.7 and 5.9) at 45°C also indicates that the charge-transfer resistance steadily increases up 3-5 hours but at 65°C (Section 5.10) it sharply increases up to 2 hours then it decreases. It is therefore inferred that the first 2-3 hours of the EW tests at this temperature range (45°C - 55°C) carried out for 4.35 and 4.97 hours (14,000 Coulombs) took place under suboptimal adsorption conditions of APAM.

4.3.2 2^{5-2} Experimental Design Results at 45°C - 65°C

As before, it is noted that Guar was dosed *twice* in this testwork and APAM was prepared in 16-fold diluted electrolyte at 50°C for 2 hours and dosed once. Table 4-15 presents the results for this experimental design.

Table 4-15: 2^{5-2} Fractional Factorial Experimental Results–Temperature Levels 45°C-65°C

	A	B	C	D=A*B	E=A*C	Mean Surface	
Run	Temp.,	C. Density	Guar	PAM	D Layer T	Roughness,	Std.
Std	°C	mA/cm^2	mg/L	mg/L	µm	Ra, µm	Dev.
1	45	28	0.50	1.00	110	5.95	0.47
2	65	28	0.50	0.50	87	6.36	0.64
3	45	32	0.50	0.50	110	7.08	1.38
4	65	32	0.50	1.00	87	5.56	0.67
5	45	28	1.00	1.00	87	5.83	0.72
6	65	28	1.00	0.50	110	6.86	2.28
7	45	32	1.00	0.50	87	5.99	0.66
8	65	32	1.00	1.00	110	5.66	0.69

The model obtained from this testwork is shown in Equation 4-20. An F-value of 2.06 implies that the model is significant. There is a 6.30% chance that the model F-value this large could occur due to noise.

Surface Roughness (µm) =

$$+6.16-0.051*A-0.089*B-0.075*C-0.41*D+0.23*E-0.17*B*C \quad (4\text{-}20)$$

It can be seen from this model that APAM D, (α=0.0041) has the most significant effect on reducing surface roughness. Diffusion layer thickness E, (α=0.1004) has the next largest effect and it increases surface roughness as expected. The effect of current density (B) and Guar (C) are insignificant (B*C, α=0.2185). Current Density B (α=0.5192), Guar C, (α=0.5855) and Temperature A, (α=0.7129) are also insignificant. The model term temperature (A) was included in the above model for completeness only; otherwise there is only 4.04% chance that the model F-value of 2.38 could occur due to noise and the probability value, α for the other model terms decrease very slightly. The regression analysis also indicates again that APAM and Guar are not aliased, APAM appears to act truly independent of Guar to reduce surface roughness[3].

The model adequacy indicated the absence of abnormalities using the graphical tests as shown previously in Section 5.3.1. Figure 4-30 shows the significant effect of APAM on surface roughness.

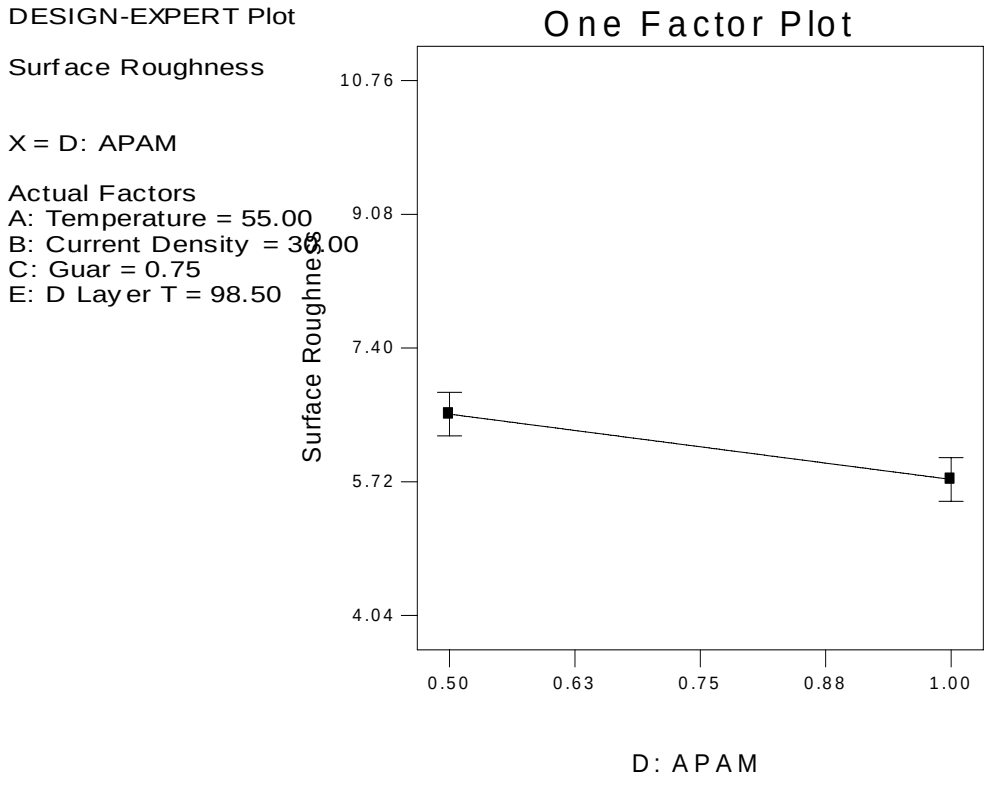

Figure 4-30: Significant Effect of APAM Concentration on Surface Roughness

It can be seen that the interaction significance of current density (B)*Guar(C) decreases from <0.0001 in the first model at 45°C-55°C to 0.2185 in the second model at 45°C-65°C. This reduction indicates that the second model is not significantly confounded in contrast to the first model. This difference is probably due to the faster degradation of Guar at 65°C than at 45°C at the same current density. This degradation process is probably true for APAM as well but if cleavage of the polyacrylamide backbone had taken place, it enhanced the reduction of surface roughness. This finding correlates with Grchev et al's.[9-11] studies on the adsorption of polyacrylamide on gold and mild steel in strong acidified solutions as follows: polyacrylamide with lower molecular weight confers higher surface coverage than polyacrylamide with high molecular weight.

4.3.3 Scanning Electron Microscopy of Electrowon Copper Deposits

Figure 4-31 – 4-38 show the Scanning Electron Micrographs (SEM) of the cross sections of the copper cathodes obtained in this test work and indicate the presence of columnar growth with small column widths of approximately 3 microns. Figure 4-32 from Run 2 at 65°C, 28mA/cm^2 current density, 0.5mg/L Guar, 0.5mg/L APAM and 87μm δ indicates the presence of voids as well as the columnar growth. Figure 4-33 from Run 3 at 45°C, 32mA/cm^2 current density, 0.5mg/L Guar, 0.5mg/L APAM and 110μm δ appears also to present some voids but its higher current density compared with Run 2 may have assisted the formation of greater number of nucleation sites.

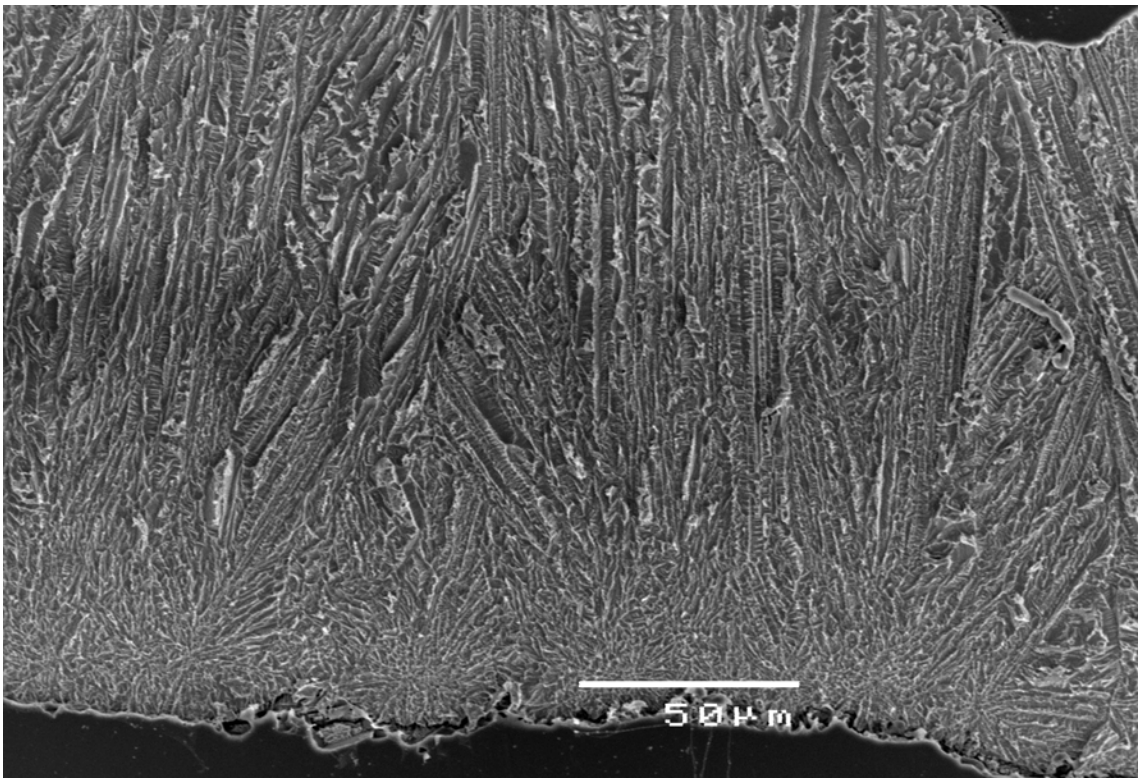

Figure 4-31: Run 1- Cross section of copper cathode obtained at 45°C, 28mA/cm2, 0.5mg/L Guar, 1mg/L APAM and 110µm δ. Surface Roughness, Ra = 5.95±0.47 microns.

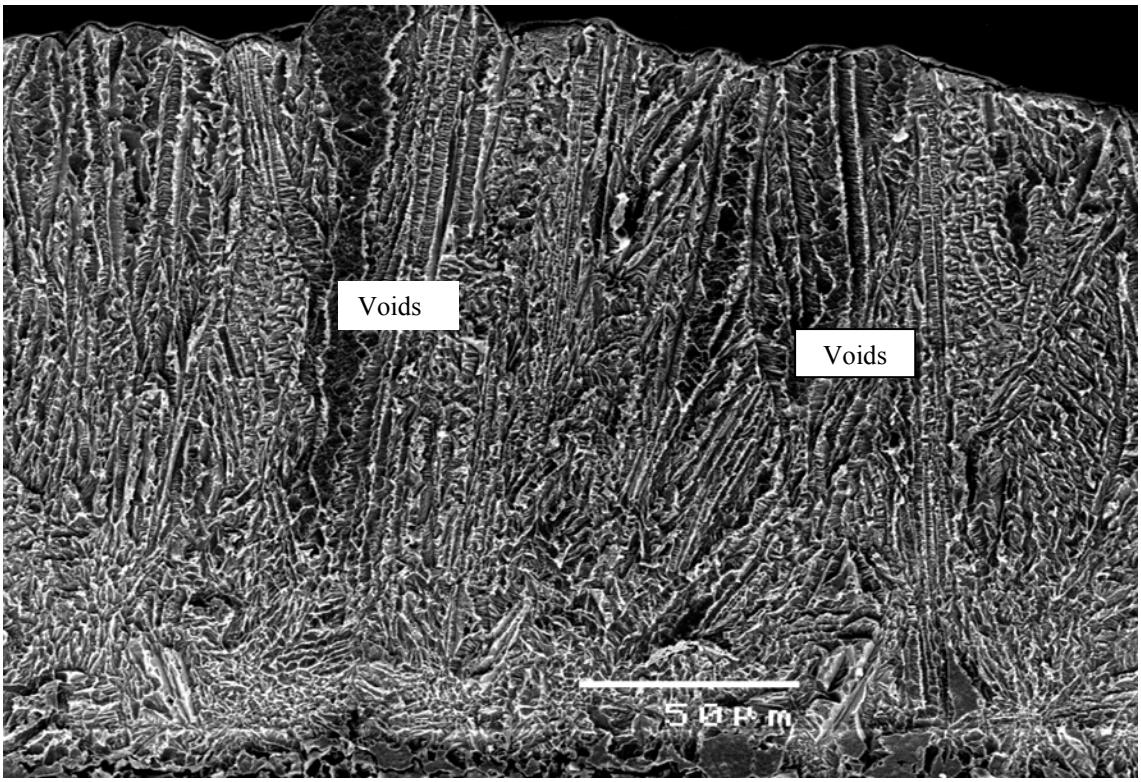

Figure 4-32: Run2 - Cross section of copper cathode obtained at 65°C, 28mA/cm2, 0.5mg/L Guar, 0.5mg/L APAM and 87µm δ. Surface Roughness, Ra = 6.36±0.64 microns.

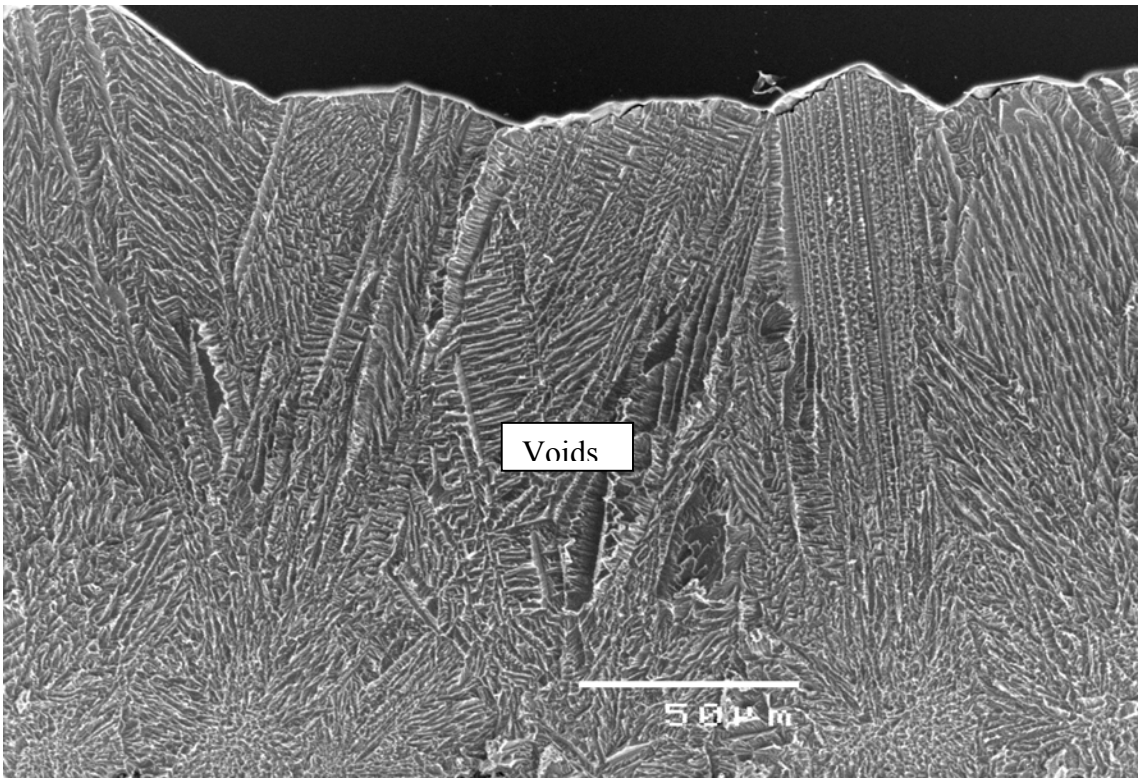

Figure 4-33: Run 3 - Cross section of copper cathode obtained at 45°C, 32mA/cm2, 0.5mg/L Guar, 0.5mg/L APAM and 110µm δ. Surface Roughness, Ra = 7.08±1.38 microns.

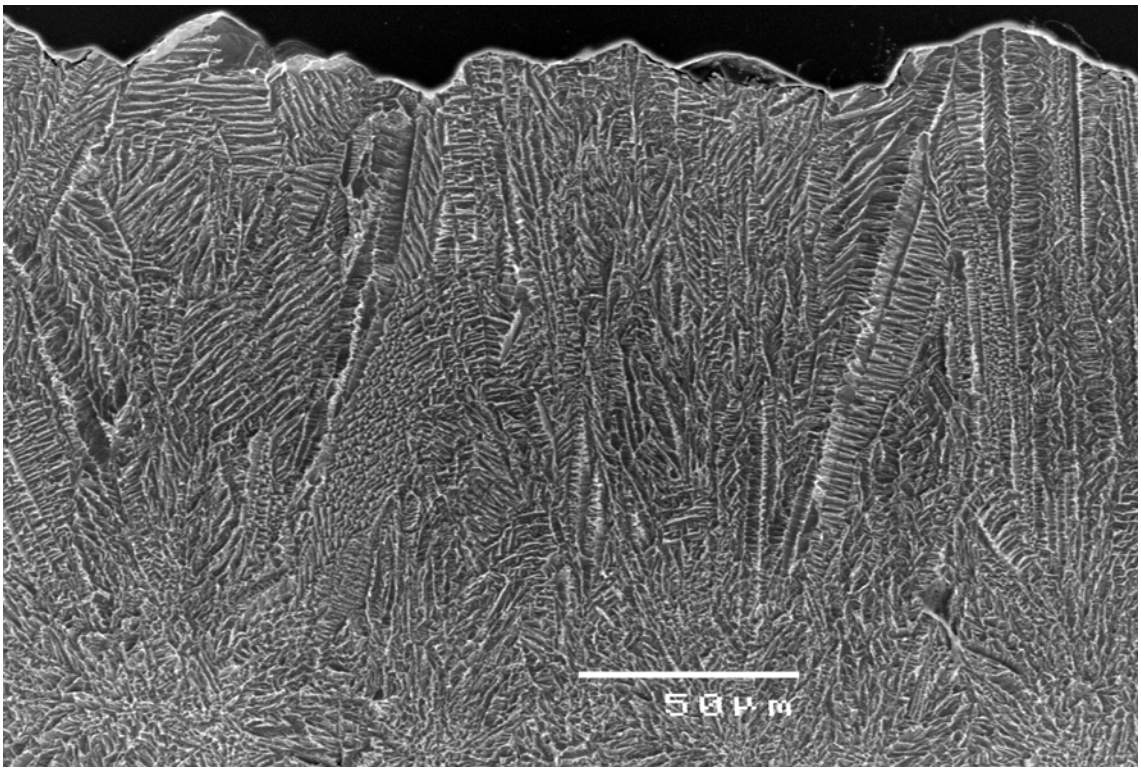

Figure 4-34: Run 4 – Cross section of copper cathode obtained at 65°C, 32mA/cm2, 0.5mg/L Guar, 1mg/L APAM and 87µm δ. Surface Roughness, Ra = 5.56±0.67 microns.

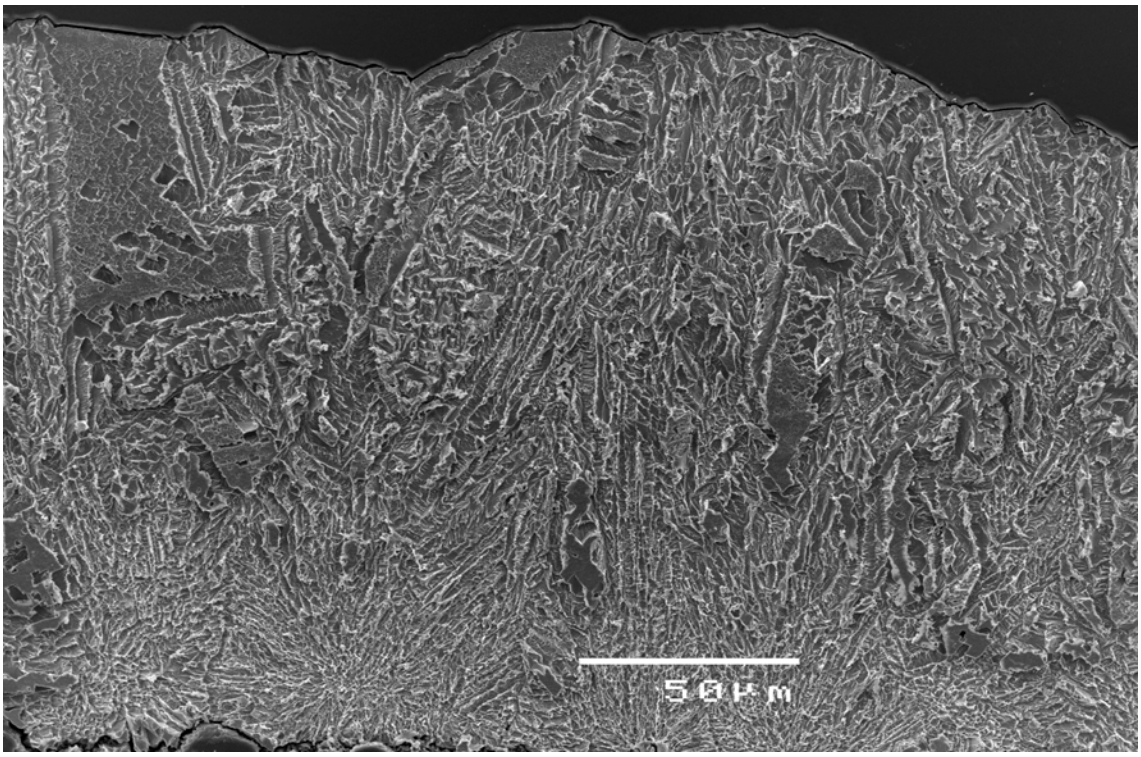

Figure 4-35: Run 5- Cross section of copper cathode obtained at 45°C, 28mA/cm2, 1mg/L Guar, 1mg/L APAM and 87µm δ. Surface Roughness, Ra = 5.83±0.72 microns.

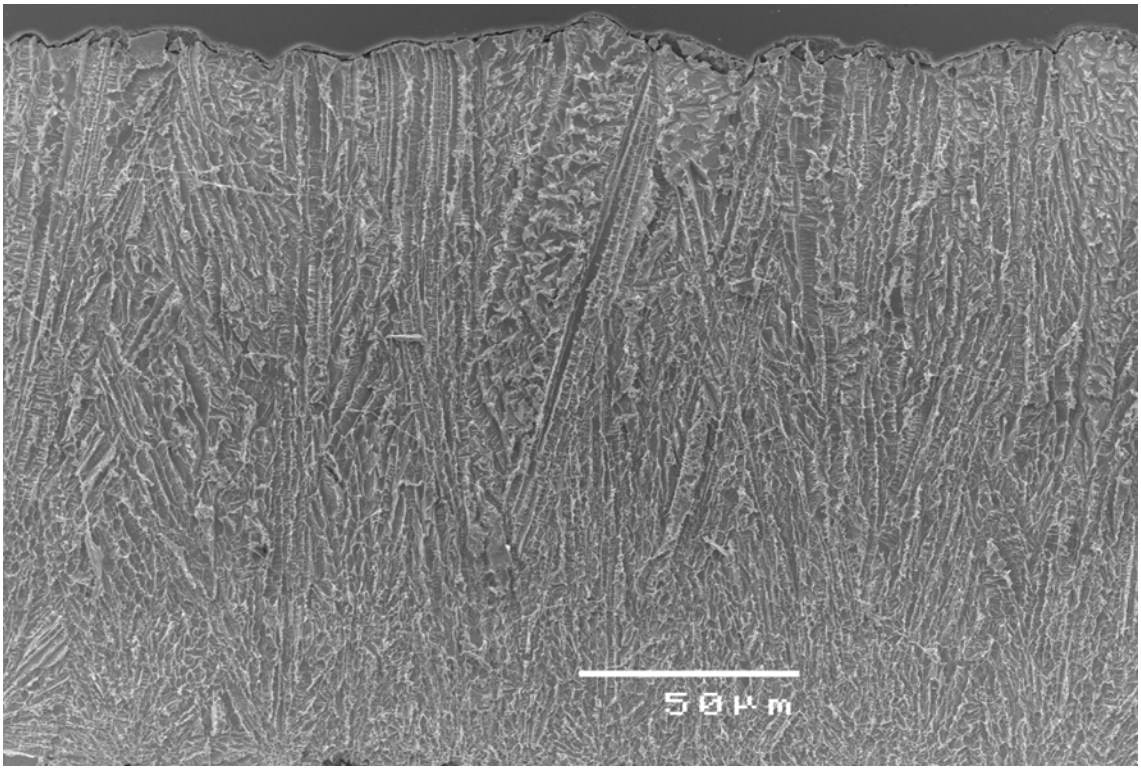

Figure 4-36: Run 6 – Cross section of copper cathode obtained at 65°C, 28mA/cm2, 1mg/L Guar, 0.5mg/L APAM and 110µm δ. Surface Roughness, Ra = 6.86±2.28 microns.

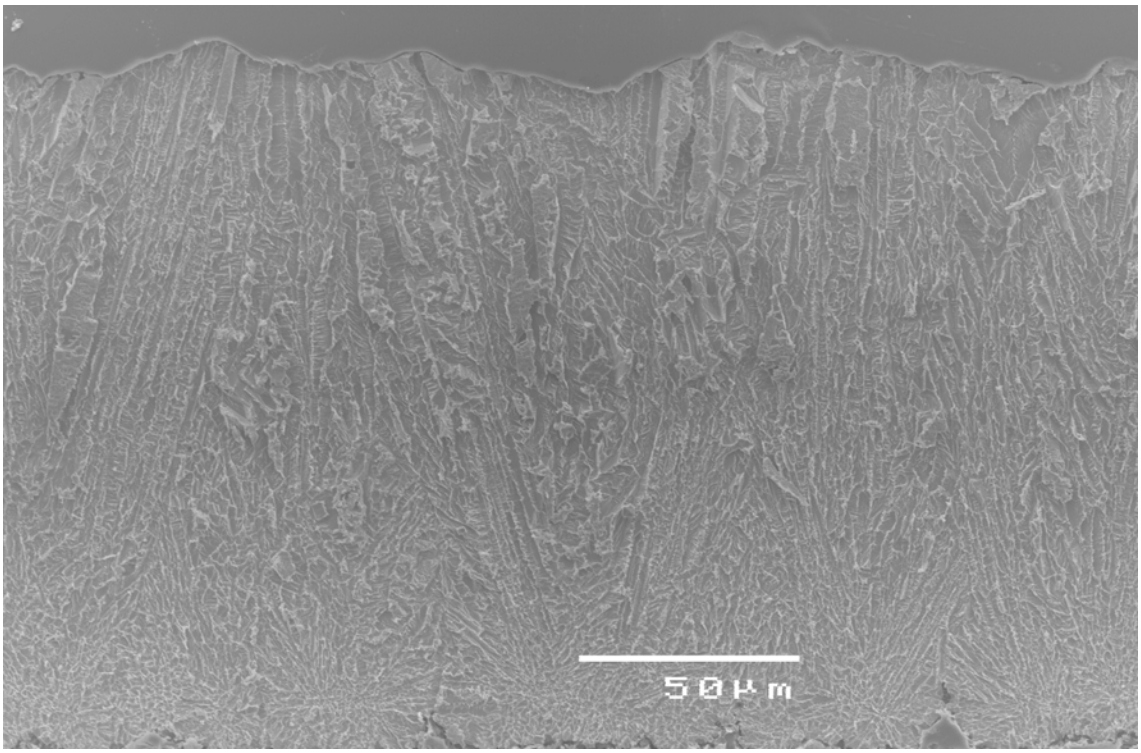

Figure 4-37: Run 7 – Cross section of copper cathode obtained at 45°C, 32mA/cm2, 1mg/L Guar, 0.5mg/L APAM and 87µm δ. Surface Roughness, Ra, = 5.99±0.66 microns.

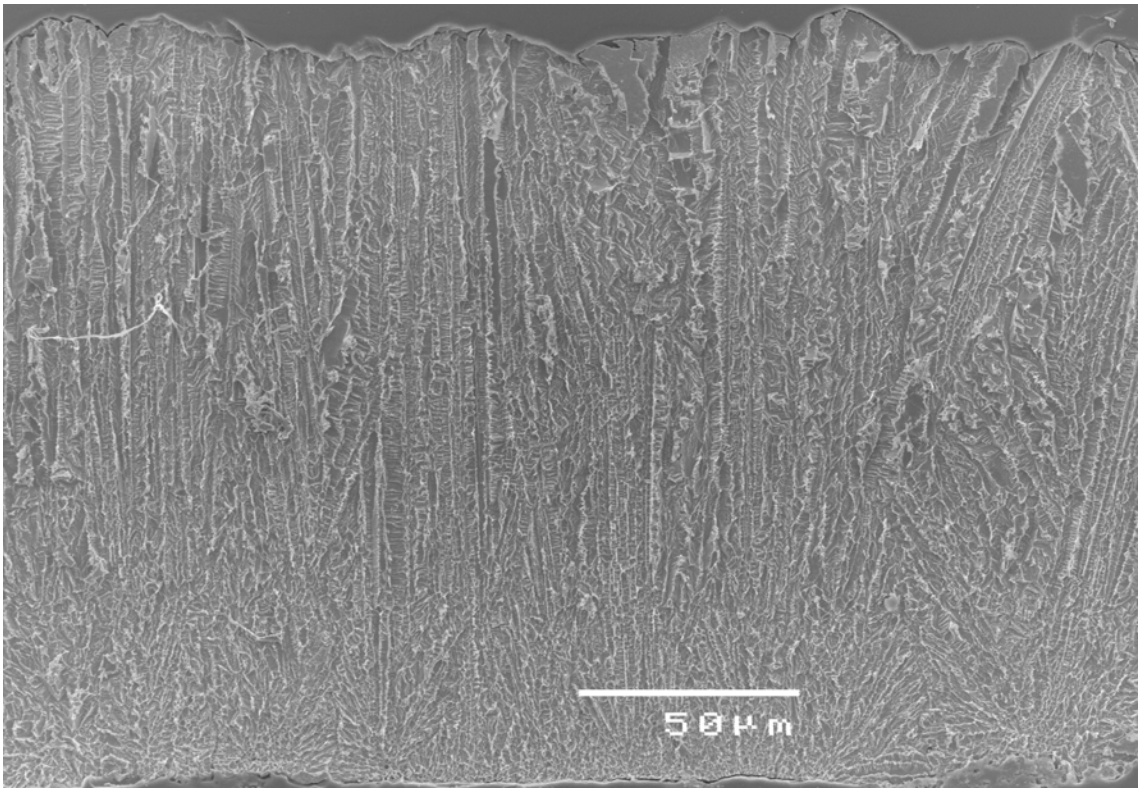

Figure 4-38: Run 8 – Cross section of copper cathode obtained at 65°C, 32mA/cm2, 1mg/L Guar, 1mg/L APAM and 110µm δ. Surface Roughness, Ra, = 5.66±069 microns.

4.3.4 Summary from Fractional Factorial Experimental Design

In conclusion, it was found that when 14,000 Coulombs were applied at 45^{o}C APAM has an insignificant effect on surface roughness, but at 65^{o}C, APAM has a significant effect in reducing surface roughness. This effect is interpreted to mean that APAM possibly achieves higher surface coverage at 65^{o}C than at 45^{o}C due to faster 'activation' and cleavage of its backbone at 65^{o}C than at 45^{o}C and therefore producing smaller molecular weights of APAM. The second conclusion drawn from these experiments is that APAM and Guar are not aliased; APAM appears to act truly independent of Guar to reduce surface roughness. Thus, APAM does not require the presence of Guar to reduce surface roughness in the concentration range 0.5 to 1 mg/L. This conclusion is further explored in the next Section.

The experiments, described in Sections 4.3.1 to 4.3.3, indicate that APAM is more effective in minimising surface roughness than Guar. A series of full factorial (2^2) experimental designs were undertaken to confirm and quantify the relative performance of APAM and Guar in controlling surface roughness.

In the following Section the effect of APAM and Guar on surface roughness, alone or in combination were studied under constant conditions of temperature, current density and RCE speed of rotation. Specifically the experiments were undertaken to.

(i) Confirm the independence of APAM and Guar by varying the the Guar to APAM systematically over 6-hours EW (Section 4.3.5),

(ii) Evaluate APAM and Guar independence using a Guar or APAM experimental design in 4.64 hours EW time (Section 4.3.6),

(iii) Re-evaluate APAM and Guar independence using Guar or APAM experimental design in 6 hours EW time (Section 4.3.7),

(iv) Confirm APAM and Guar independence using Guar or APAM in 12 hours EW time (Section 4.3.8).

4.3.5 2^2 Experimental Design – APAM *to* Guar Ratio at 50°C and 6-Hours EW Time

It was concluded in Section 4.3.4 that Guar and APAM act independently of ane another in affecting surface roughness. To confirm the independence of APAM and Guar on surface roughness the Guar to APAM ratio was expanded under fixed conditions of current density, temperature and diffusion layer thickness. A statistically significantly different surface roughness given by a specific ratio would indicate their dependence; otherwise, their independence indicated in the previous Sections will be confirmed.

Guar was dosed *twice* and APAM was dosed *only once*. The first dose of Guar was 20 minutes before EW time and the second dose at 2-hours and 50 minutes (or half of the total residence time of Guar in the electrolyte) after the EW cell was powered. The other EW conditions are in Table 4-16.

Table 4-16: Electrowinning Conditions for APAM-to-Guar Ratio

Current Density, A/m^2	300
Electrolyte Temperature, °C	50
Diffusion Layer Thickness, μm (10rpm)	109
Electrowinning Time, Hrs	6
Number of Coulombs per cm^2	650

A 2^2 full factorial design was used to expand the APAM to Guar concentration ratio from Sections 4.3.1 and 4.3.2. Therefore while the APAM/Guar low and high level ratios were set at 0.5 and 1.5; the low and high levels for Guar concentration were set at 0.25 and 1mg/L. This experimental design systematically increases the APAM concentration as shown in Table 4-17. The conditions were selected to clarify further whether an increased proportion of either Guar to APAM and APAM to Guar, i.e., 1.5/1, can reduce effectively surface roughness in an extended electrowinning time. The 2^2 experimental design and results for the Guar to APAM ratio are shown in Table 4-17 and Figure 4-39.

Table 4-17: 2^2 Experimental Design and Results for APAM-to-Guar Ratio

	Factors		Calculated Concentration	Surface Roughness, Ra, µm		Number Peaks-per-Centimeter	
Run	A=APAM/Guar	B=Guar,mg/L	APAM, mg/L	Mean	Std. Dev.	Mean	Std. Dev.
1	0.5	0.25	0.125	6.05	0.48	86	7.80
2	1.5	0.25	0.375	6.62	0.51	83	10.14
3	0.50	1	0.5	6.54	0.29	83.88	8.84
4	1.5	1	1.5	6.28	0.44	84.50	5.96

A model shown below as Equation (4-21) was obtained from this testwork with an F-value of 2.79 that implies that the model is significant. There is only a 5.91% chance that the model F-value this large could occur due to noise.

$$\text{Surface Roughness } (\mu\text{m}) = 6.37 - 0.21 * A * B \qquad (4\text{-}21)$$

The model indicates that A (APAM/Guar) and B (Guar) are confounded and significantly (α=0.0123) reduce the surface roughness. However, it could be deduced that APAM causes this effect since [(APAM/Guar)*Guar = APAM].

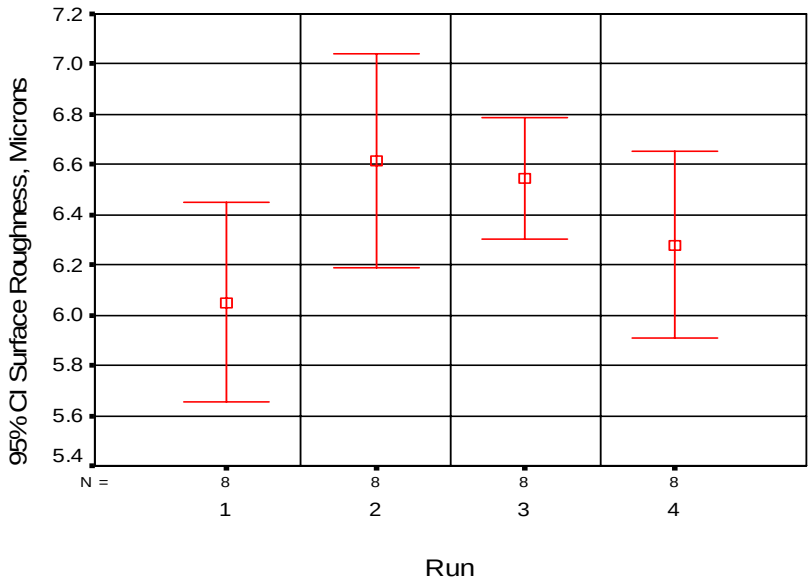

Figure 4-39: Error Box Plot of the Effect of APAM-to-Guar Ratio on Surface Roughness. Run 1 – Guar 0.25mg/L and APAM 0.125mg/L, Run 2 – Guar 0.25mg/L and APAM 0.375mg/L, Run 3 – Guar 1mg/L and APAM 0.5mg/L and Run 4 – Guar 1mg/L and APAM 1.5mg/L

Figure 4-40 shows the confounded and significant factors A (APAM/Guar) and B (Guar) indicating the effect of the APAM/Guar ratio and the Guar concentration on

the surface roughness. Low APAM/Guar ratio and low Guar concentration gave lower surface roughness values although their mean values are not significantly different. Figures 4-42, 4-43, and 4-44 show the diagnostic graphs validating the model.

Figure 4-40 shows the significant aliased term and indicates that an increase in Guar concentration increases surface roughness. The surprising and detrimental effect of Guar concentration on surface roughness noted in Figure 4-26 – Section 4.3.1 was replicated in these tests. Figure 4-40 also indicates that an increase of the APAM to Guar ratio appears to increase the surface roughness. As this last result is apparently contradictory with Section 4.3.2 – Figure 4-30, it is inferred that the presence of Guar in the electrolyte bath is altering the effect of APAM on surface roughness. In summary it has been shown that the overall results of this Section agree with those of Sections 4.3.1 and 4.3.2 in that Guar appears to increase surface roughness and, in contrast, APAM appears to decrease it. Therefore the effect of Guar and APAM on surface roughness should be investigated *separately*, as described in the following Sections.

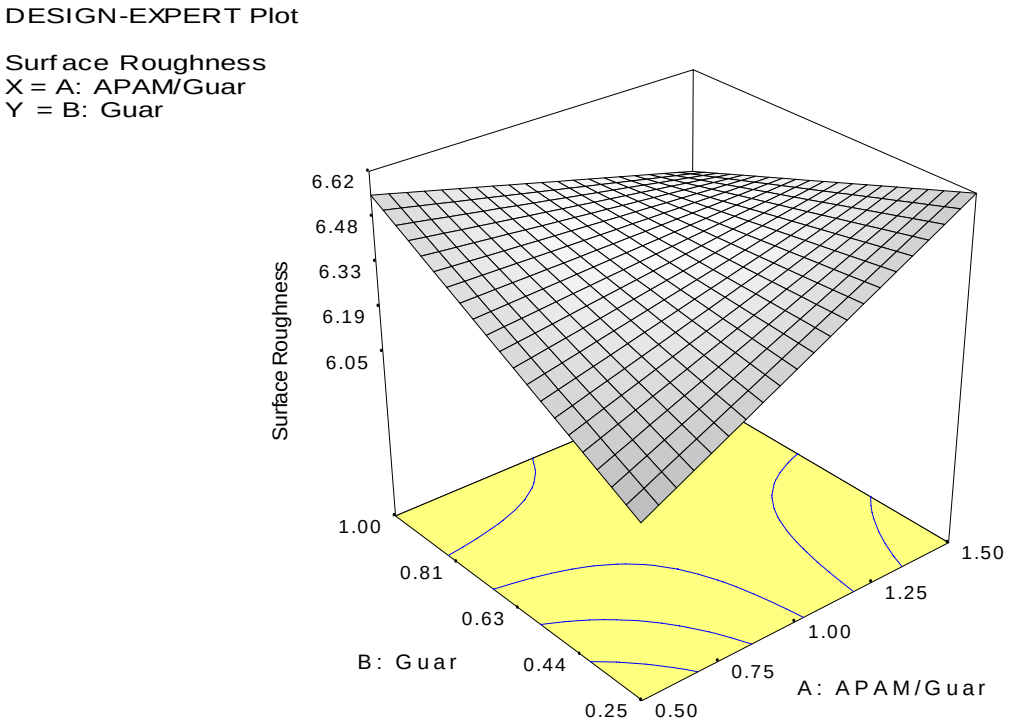

Figure 4-40: Significant Effect of APAM/Guar Ratio and Guar on Surface Roughness
A: [APAM/Guar], B: Guar, mg/L and Surface Roughness, µm

The concept of Peaks-per-Centimeter (PPC) is introduced to evaluate more closely the surface profile in the presence and absence of APAM and Guar. PPC is defined as the number of roughness profile elements per centimeter which consecutively intersect a specified upper profile section level and a lower profile section. The Mahr M1 Perthometer gives the surface roughness and PPC readings simultaneously. Figure 4-41 shows that for these experiments none of the PPC is significantly different.

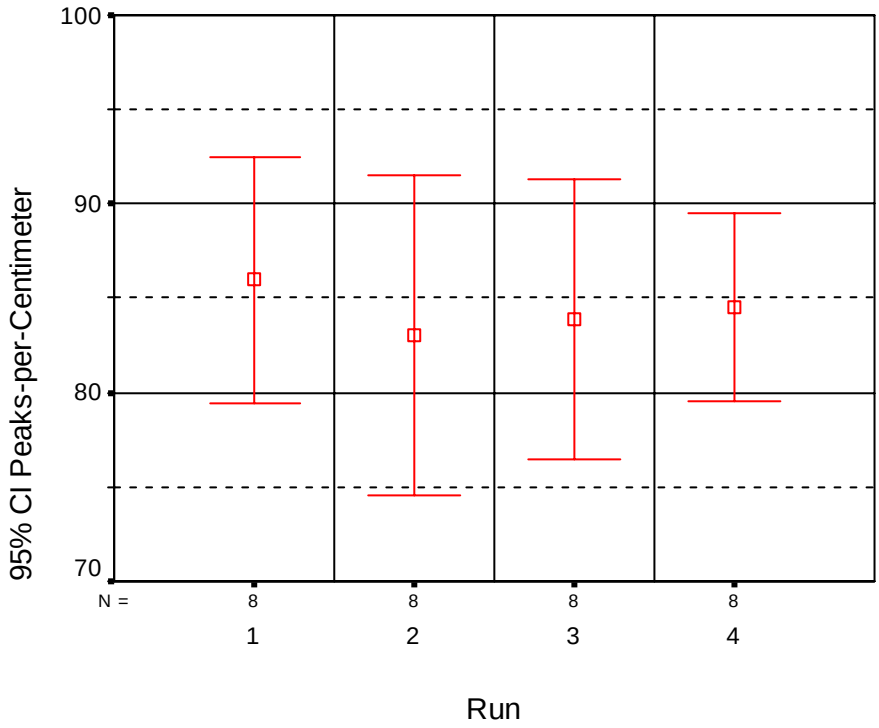

Figure 4-41: Error Box Plot of the Effect of APAM-to-Guar Ratio on PPC. Run 1 – Guar 0.25mg/L and APAM 0.125mg/L, Run 2 – Guar 0.25mg/L and APAM 0.375mg/L, Run 3 – Guar 1mg/L and APAM 0.5mg/L and Run 4 – Guar 1mg/L and APAM 1.5mg/L.

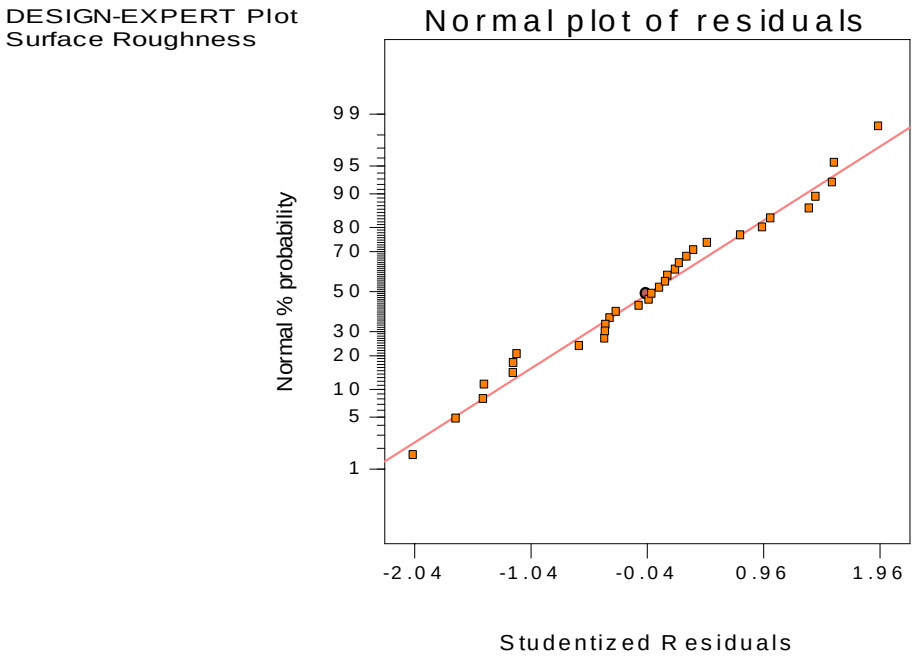

Figure 4-42: Studentized Residuals Plot

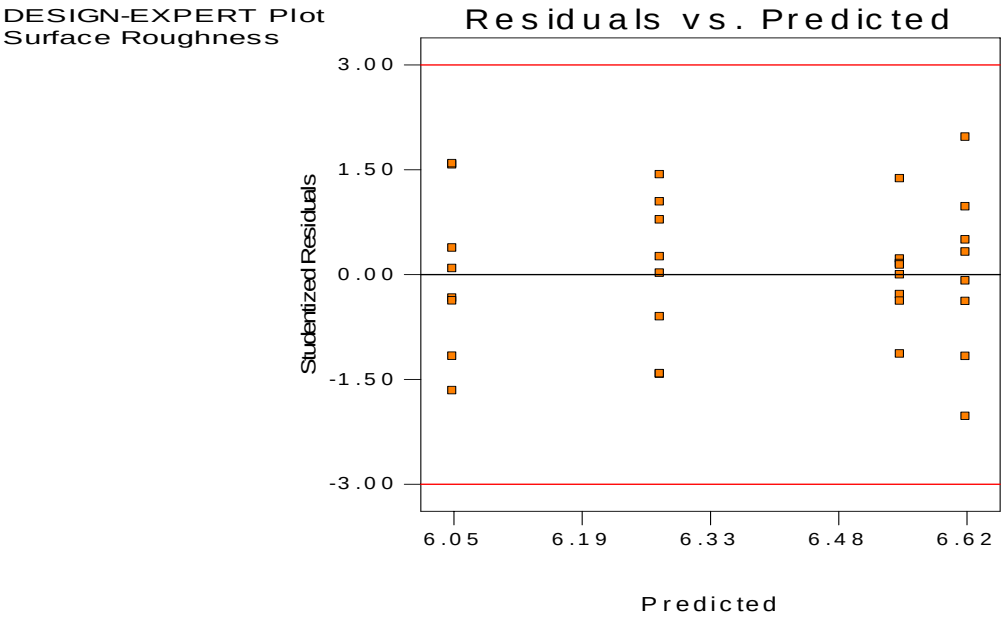

Figure 4-43: Residuals vs. Predicted Plot

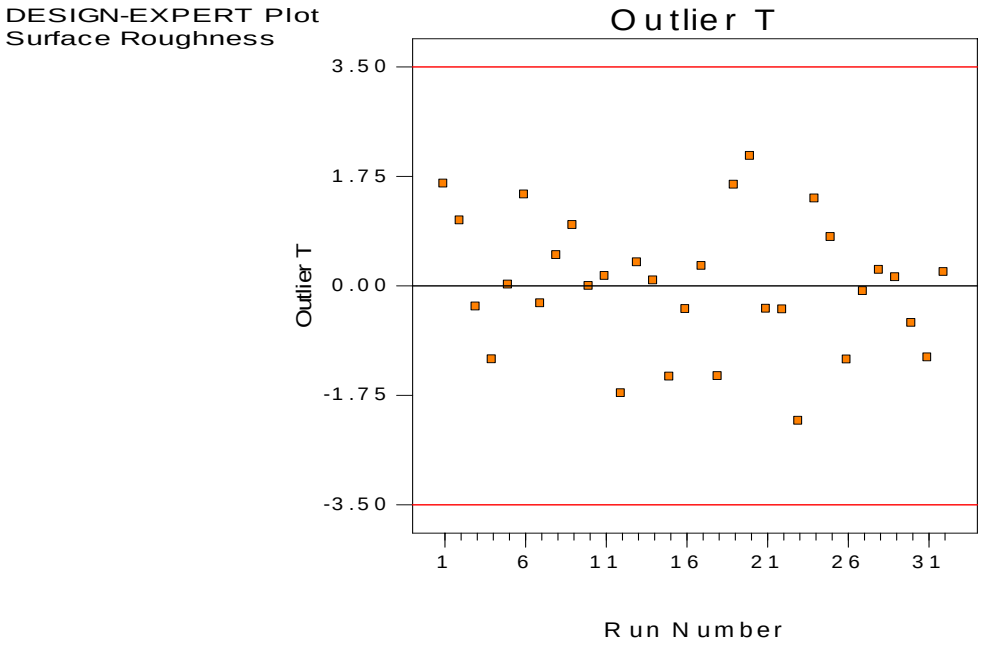

Figure 4-44: Outlier T Diagnostic Plot

4.3.6 2^2 Experimental Design APAM or Guar at 50°C and 4.6 Hours EW Time

A 2^2 full factorial design was used to evaluate the whether Guar *or* APAM is the most effective additive to control surface roughness. The temperature (50°C), current density (300A/m^2), RCE speed of rotation (17.5rpm) and the EW time were selected to be close of the mid-point of those used in Section 4.2. (Table 4-18). Both Guar and APAM were dosed *only once* at the beginning of each test.

Table 4-18: Electrowinning Conditions for APAM or Guar

Current Density, A/m^2	300
Electrolyte Temperature, °C	50
Diffusion Layer Thickness, µm	97.5
Electrowinning Time, Hrs	4.64
Number of Coulombs per cm^2	500

Table 4-19 present the 2^2 experimental design and their results in terms of surface roughness and Peaks-per-Centimeter (PPC). Figures 4-45 and 4-46 depict the surface roughness and PPC shown in Table 4-19.

Table 4-19: 2^2 Guar-or-APAM Experimental Design and Results

	Factors		Surface Roughness, Ra, μm		No. Peaks-per-Cm.	
Run	Guar,mg/L	APAM,mg/L	Mean	Std. Dev.	Mean	Std. Dev.
1	0.50	0.50	5.19	0.47	101.13	10.26
2	0.00	0.00	4.70	0.36	104.13	7.59
3	0.00	1.00	5.33	0.48	94.38	8.72
4	1.00	0.00	5.08	1.10	95.88	20.65
5	1.00	1.00	5.01	0.16	103	8.62

In this Section, PPC assists more clearly than surface roughness to explain the initial stages of dendrite formation in the absence of additives. The result on surface roughness in the *absence* of Guar or APAM is inconsistent with the general effect of an organic additive on nucleation and growth determining the smoothness of the deposit.

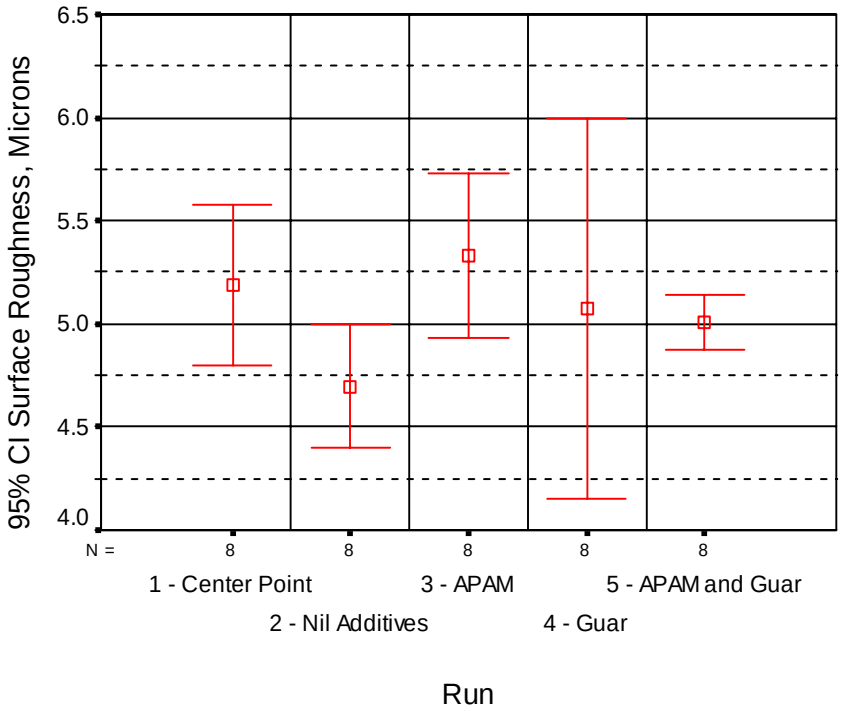

Figure 4-45: Error Bar Plot of Surface Roughness, Ra, μm after 4.64-Hours EW Time. Run 1 - Center Point, 0.5mg/L APAM and 0.5mg/L Guar; Run 2 – Nil additives; Run 3 – 1mg/L APAM; Run 4 – 1mg/L Guar and Run 5 – 1mg/L both APAM and Guar.

This finding appears to be due to the initial formation of dendrites, very fine needles, since two deposits can be obtained with the same surface roughness but with different numbers of PPC.

Table 4-19 and Figures 4-45 and 4-46 indicate that Run 2 in the absence of additives gave the lowest surface roughness and highest PPC value after 4.64-hours EW time or 500 Coulombs per square centimeter.

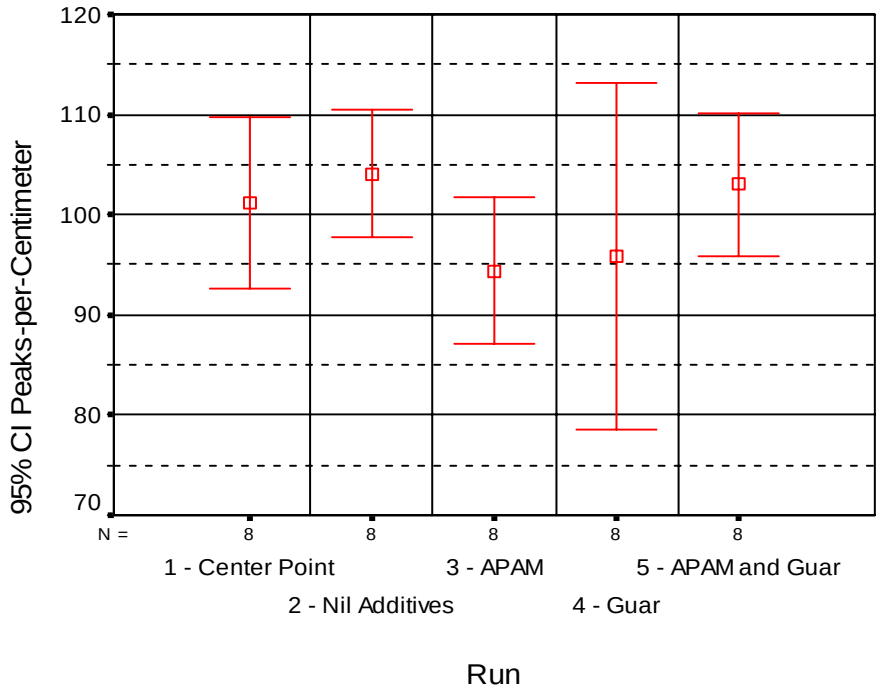

Figure 4-46: Error Bar Plot of PPC after 4.64-Hours EW Time. Run 1 - Center Point, 0.5mg/L APAM and 0.5mg/L Guar; Run 2 – Nil additives; Run 3 – 1mg/L APAM; Run 4 – 1mg/L Guar and Run 5 – 1mg/L both APAM and Guar.

The finding in this thesis is similar to that of Szymanski et al.[12] who studied the copper morphology in the absence of additives using Atomic Force Microscopy (AFM) mimicking industrial electrorefining conditions in terms of temperature (65^{o}C), current densities (21.3 and 25.3mA/cm^2), copper concentration (40g/L) but the concentration of sulphuric acid was not reported. It was concluded that in the early stages of electrodeposition, the *surface roughness was smalle*r when 25.3mA/cm^2 was used than when 21.3mA/cm^2 was used. However, the surface roughness increased faster with time at 25.3mA/cm^2 current density than at 21.3mA/cm^2 and hence time-scaling

modelling indicated that rougher copper deposit will be produced at the high current density than those at the low current density for 7 days plating.

It can be seen also from Figure 4-46 that the standard deviation for Guar alone experiments (Run 4) is markedly greater than those observed in the presence of APAM (Run 3). This result indicates the non-uniformity of the surface roughness in the presence of Guar alone. In contrast, APAM produced a more uniform copper deposit than Guar. This result indicates that Guar reacts faster and loses its levelling efficacy faster than APAM. Therefore, Guar needs to be dosed at least twice for every five hours of EW time or constantly to maintain efficacy. The physical appearance of the copper deposit obtained from this EW test with Guar and APAM at 1mg/L concentration was smooth and uniform. However, when Guar alone was present in the electrolyte, some convective lines on the copper deposit and some holes in the coper deposits (~3 spots of ~1x~1mm) were observed.

It is therefore concluded that EW time is critical to the evaluation of surface roughness. A regression model for the conditions stated in this section can be misleading due to the complex behaviour of the surface roughness and PPC at early stages of electrodeposition in the absence of additives. Therefore such a model was not presented. Nevertheless, the 2^2 experimental testwork at conditions of temperature (50^oC), current density ($300A/m^2$), 17.5rpm speed of rotation and 4 hours 38 minutes qualitatively indicated that APAM produces a more uniform surface roughness than Guar when both were *dosed once* only since APAM shows lower surface roughness standard deviation than Guar.

At the early stages of EW and in the absence of additives (i) the number of PPC was higher than in the presence of Guar and APAM and (ii) surface roughness at early stages can be smaller at higher current density, e.g., 25-30 mA/cm^2 than at lower current density, e.g., 20-25mA/cm^2 current densities. In Section 4.3.7 below it will be shown that the smaller surface roughness and high PPC and in the absence of additives is in a transition stage for the deterioration of the surface profile at 6-hours EW time.

4.3.7 2^2 Experimental Design – APAM or Guar at 50°C and 6 Hours EW Time

This test was conducted to continue evaluating the effectiveness of the additives Guar or APAM, either alone or in combination, on surface roughness and PPC over 6-hours of EW time. Guar was dosed *twice* and APAM *once.* The electrolyte temperature, current density and rotational speed of the electrode were 50°C, 300A/m^2 as in the previous Section and the RCE had a rotation of speed of 10 rpm. The experimental design and results are shown in Table 4-20.

Table 4-20: 2^2 Experimental Design APAM-or-Guar at 10 RPM - 50°C - 6 Hours EW

	Factors, mg/L		Surface Roughness, Ra, μm		No. Peaks per Centimeter		Observations
Run	APAM	Guar	Mean	Std. Dev	Mean	Std.Dev	Small Needles
1	0	0	7.68	2.16	65.13	13.95	Numerous
2	0	1	5.85	0.52	94.38	12.32	1big+Many
3	1	0	6.42	0.27	82.75	8.24	None
4	1	1	6.71	0.36	83.38	7.46	None
2R	0	1	6.48	0.70	87.63	8.35	Numerous nascents

The Model F-value of 9.96 for the number of PPC implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In this case A and A*B are significant model terms as shown in Equation 4-22.

$$\text{Number of Peaks-per-Centimeter} = 81.41 + 7.47 * A + 1.66 * B - 7.16 * A * B \quad (4\text{-}22)$$

This model predicts that Guar (A, $\alpha<0.0006$) has a most significant effect to increase the number of PPC than APAM (B, $\alpha = 0.3948$). Guar*APAM (A*B, $\alpha = 0.0009$) has a significant effect to reduce PPC. Figure 4-47 shows these effects in an error box plot with 95% CI and Figure 4-48 in a 3D plot. The highest number of PPC shown in Figure 4-46 in the absence of additives decrease to the lowest number of PPC in Figure 4-47. This result confirms the conclusions made in Section 4.3.6.

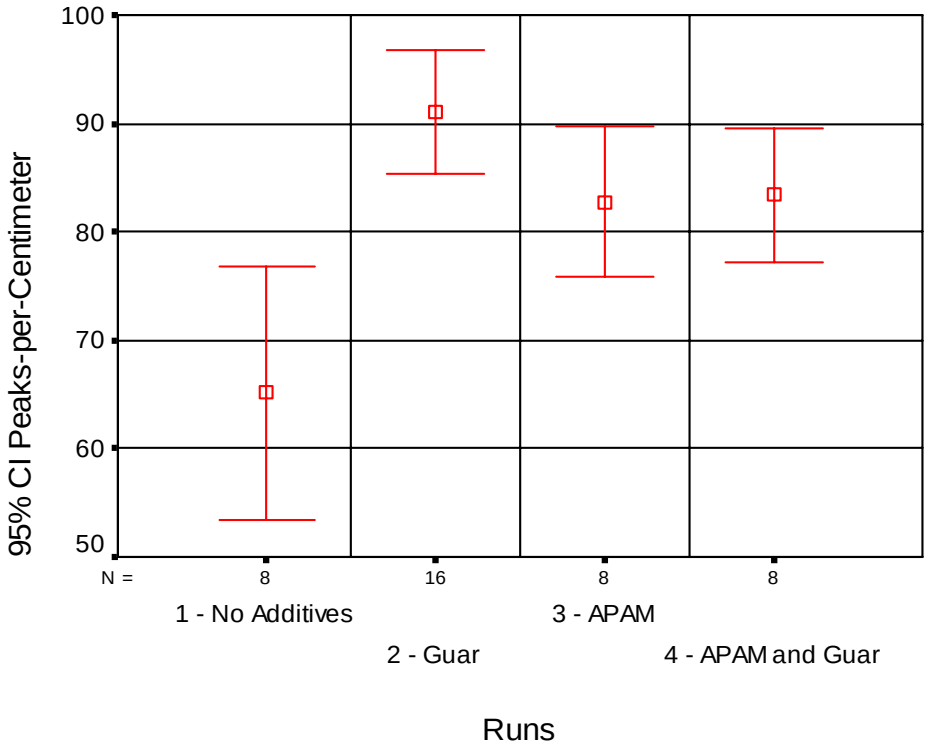

Figure 4-47: Effect of Guar or APAM on PPC after 6-Hours. EW Time

Table 4-20 shows that dendrite formation is uncontrollable from Run 2 and its replicate (2R) with Guar only. It indicates that the PPC for nil additives is statistically lower compared with those for Guar or APAM, alone or in combination. It also appears that the number of PPC for Guar is higher compared with those for Guar and APAM, and APAM alone. This observation implies that at longer EW time than 6-hours, the surface roughness with Guar should be deteriorated further.

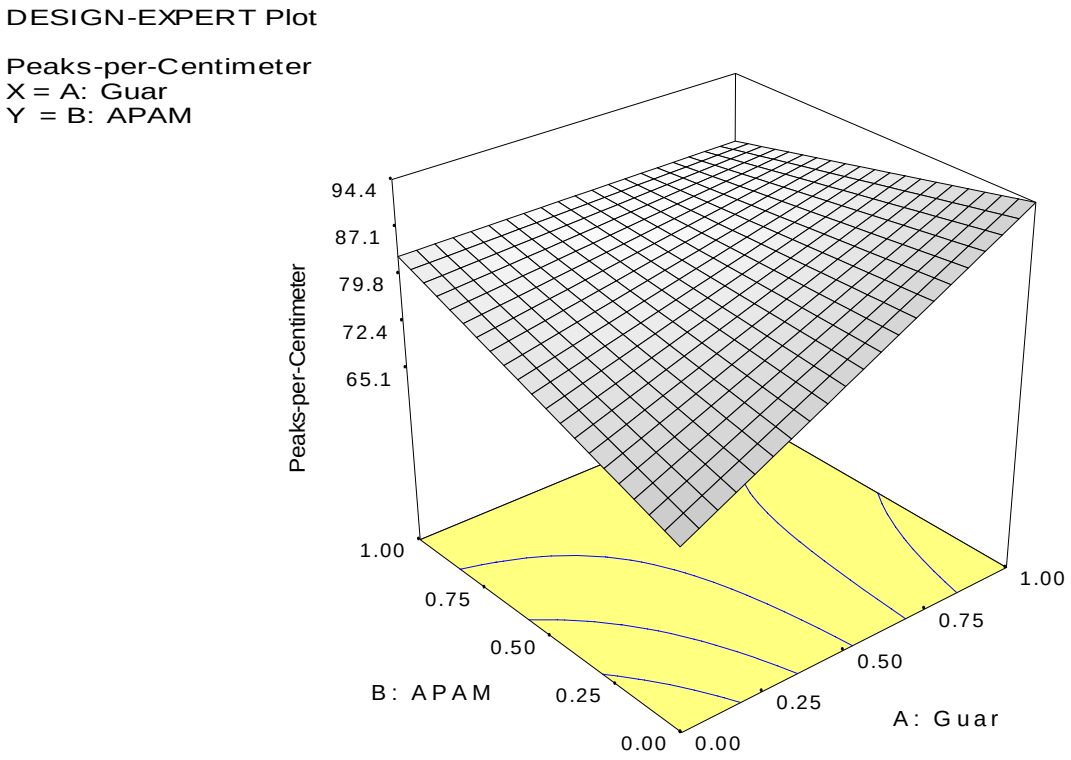

Figure 4-48: The Significant Effect of Guar and APAM on PPC after 6-Hours EW Time

Equation 4-23 shows the surface roughness model for this testwork.

$$\text{Surface Roughness } (\mu\text{m}) = 6.66 - 0.38 * A - 0.098 * B + 0.53 * A * B \quad (4\text{-}23)$$

The Model F-value of 3.64 for surface roughness implies the model shown in Equation 4-23 is significant. There is only a 2.48% chance that a "Model F-Value" this large could occur due to noise. The aliased term (Guar*APAM, $\alpha = 0.0134$) has the most significant effect on increasing surface roughness. Guar, (A, $\alpha = 0.0648$) has a weak effect on reducing surface roughness. APAM (B, $\alpha=0.6271$) has an insignificant effect on reducing surface roughness.

This surface roughness model indicating that Guar (A) has stronger effect than APAM (B) on reducing surface roughness may be misleading. Such a statistical model does not incorporate the complex mechanism of the early stages of dendrite formation in which initially passes through a period of smoother surface roughness and higher

number of PPC in the absence of both Guar and APAM which is followed by high surface roughness and dendrite formation quantitatively. Guar leads to dendrite formation as shown in Table 4-20. Moreover, no dendrites were observed from runs 3 and 4 in which APAM were present.

The PPC model, Equation 4-23, however, appears to predict that Guar produces higher PPC than APAM. It is therefore concluded that high number of PPC leads to the deterioration of the surface roughness profile as shown with nil additives at 4.64-hours EW time (Figure 4-46) and with Guar at 6-hours EW time (Figure 4-47). It is therefore inferred that the PPC obtained with Guar at longer EW time greater than 6-hours, must decrease. In other terms the surface roughness must become dendritic at 12-hours EW time. This behaviour will be shown in the next Section 4.3.8.

Figure 4-49 to 4-53 show the Scanning Electron Microscopy (SEM) micrographs of the copper cathodes. These micrographs show the electrolyte face for all runs. The line-scale is 50μm except Run 2 for which line-scale is 100μm. All micrographs show angled pyramidal crystal growth as reported in the recent literature[13-15] in the presence of animal glue and chloride ions. It is seen that the nucleation and growth is different in the presence and absence of organic additives. Figure 4-49 shows the presence of very small crystallites in the absence of additives but these crystallites are not observed in the presence of additives. The presence of small crystallites in the absence of additives agrees with the findings from recent studies using in-situ AFM on copper electrodeposition indicating that in the absence of PEG, chloride ions and Janus Green B (JGB) and bis(3-sulphopropyl) disulphide (SPS) copper deposition follows a progressive nucleation and 3D diffusion-limited growth[16]. Moreover, the nucleus density for solutions in the absence of additives were about an order of magnitude larger than those containing additives at any given potential, illustrating that the additives influence the nucleation rate.

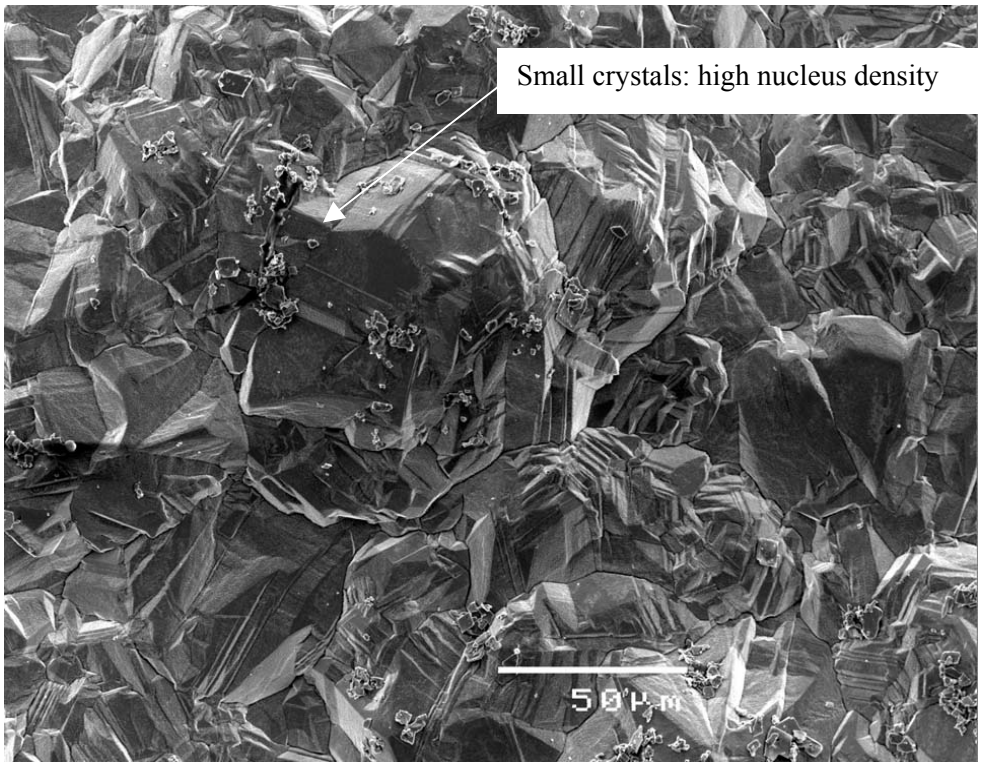

Figure 4-49: Run 1 - No Additives

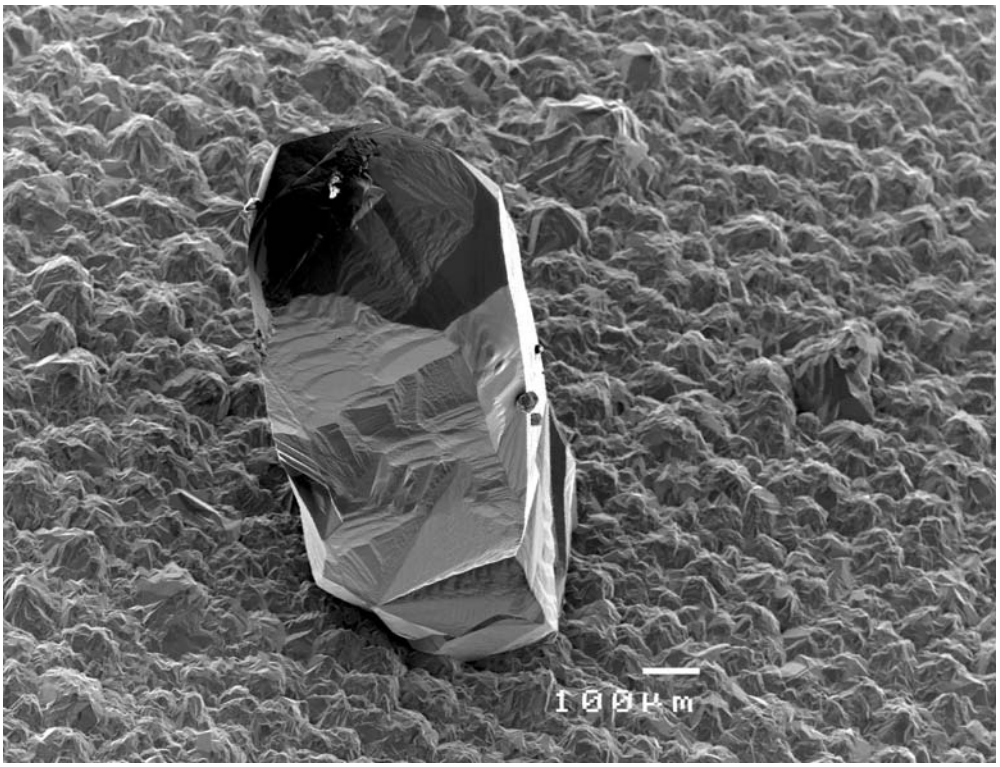

Figure 4-50: Run 2 – Guar Only

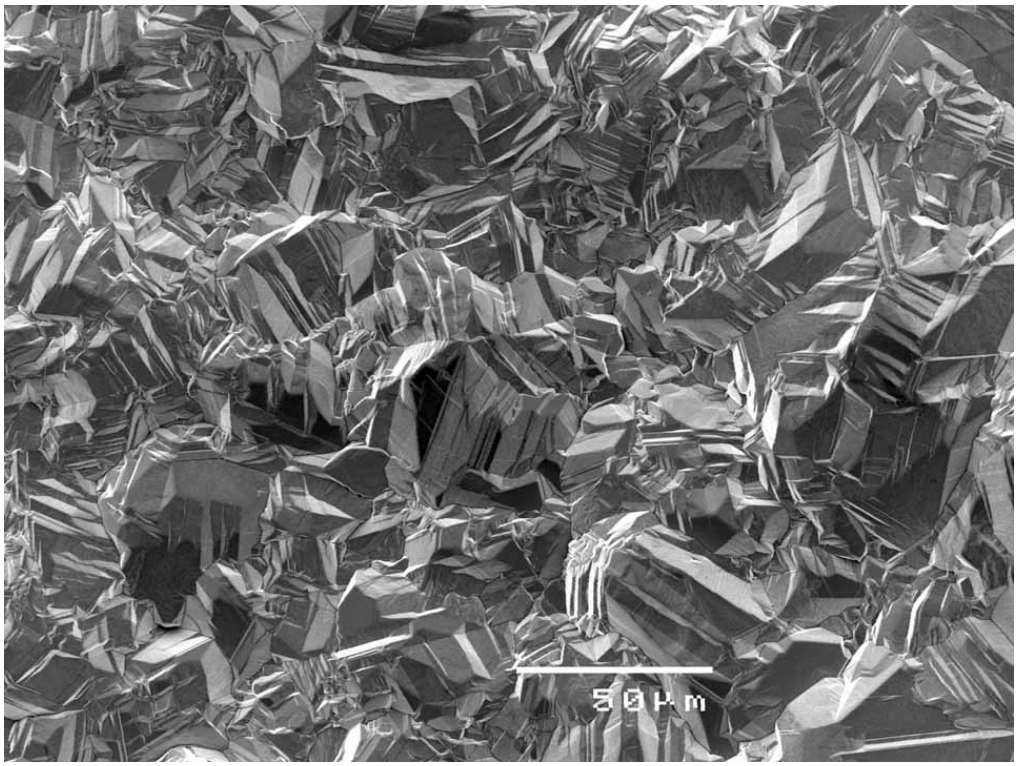

Figure 4-51: Run 2R – Guar Only

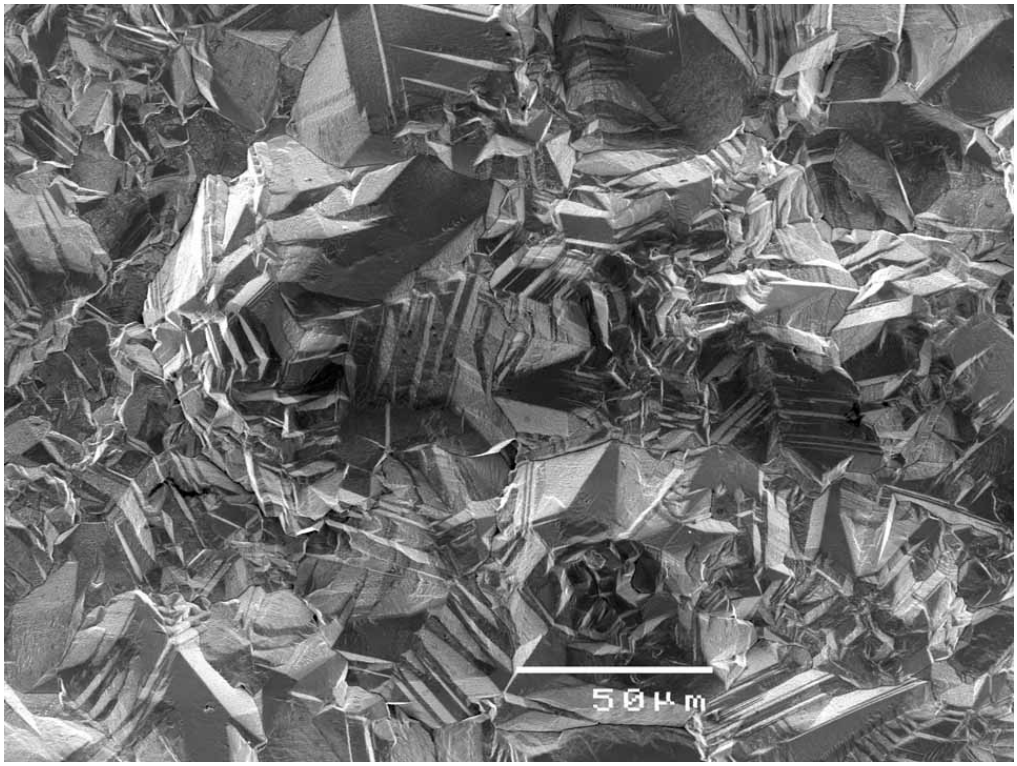

Figure 4-52: Run 3 – APAM Only

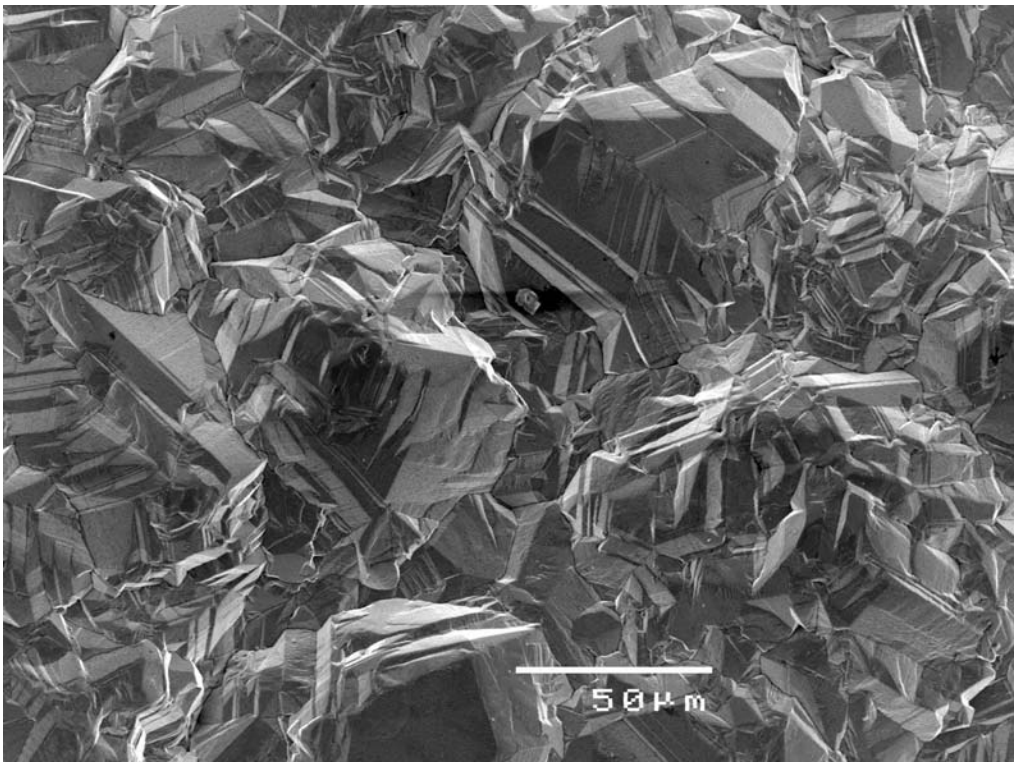

Figure 4-53: Run 4 – APAM and Guar

4.3.8 APAM or Guar at 50°C for 12 Hours EW Time

This test was conducted to compare APAM with Guar over 12 hours EW time to clearly resolve whether APAM produces smoother surface roughness than Guar as demonstrated in previous Section over 6 hours EW time. One mg/L Guar was dosed at 0 (20 minutes before the current was applied to the EW cell), 3, 6 and 9 hours giving a total cumulative concentration of 4 mg/L over 12 hours EW time. In Test 132 APAM was dosed o*nly once* at 20 minutes before the EW was powered, in Test 133, APAM was *dosed twice* at 0 and 6 hours over 12 hours EW time.

The experimental conditions and results are shown in Table 4-21 and Figures 4-54 and 4-55 and clearly reconfirm *all* previous tests that APAM is the most effective organic additive to control dendrite growth than Guar, the industry-standard additive.

Table 4-21: Effectiveness of Guar and APAM to Control Dendrite Growth

ADDITIVE	**Guar**	**APAM**	
RCE Test No.	128	132	133
PAM Prep. Residence Time, Hrs	2	2	2
Guar or PAM Preparation Media	water	16-fold DE	16-fold DE
Guar or PAM Preparation Temp., ^{o}C	25	50	50
Guar or APAM Initial Conc., mg/L	1	1	1
Guar or APAM Dosed, mg/L	1	1	1
Guar or APAM Dosing Frequency, Hrs	3	0	6
Guar or APAM Total Dosed, mg/L	4	1	2
Diffusion layer Thickness, µm (10rpm)	92	92	92
Electrowinning Time, Hrs	12	12	12
Current Density, Amp/m^2	300	300	300
Electrolyte Temperature, ^{o}C	50	50	50
No. Coulombs/cm^2	1300	1300	1300
Surface Roughness, Ra, µm	*Unmeasurable*	12.79	11.71
Surface Roughness Std. Dev., µm	*NA*	1.07	1.28
Number of Dendrites > 0.1mm	12	*Nil*	*Nil*

The surface roughness of the copper deposit obtained from the testwork with Guar was not able to be determined since the stylus gets stuck on the dendrites. In contrast, the surface roughness of the copper cathodes produced with APAM was still measurable even though only one and two mg/L were dosed for 12-hours EW time. This finding confirms that the ageing products of APAM are more effective than those of Guar and therefore it is consistent with the hypothesis that the APAM surface coverage is much higher than the Guar surface coverage.

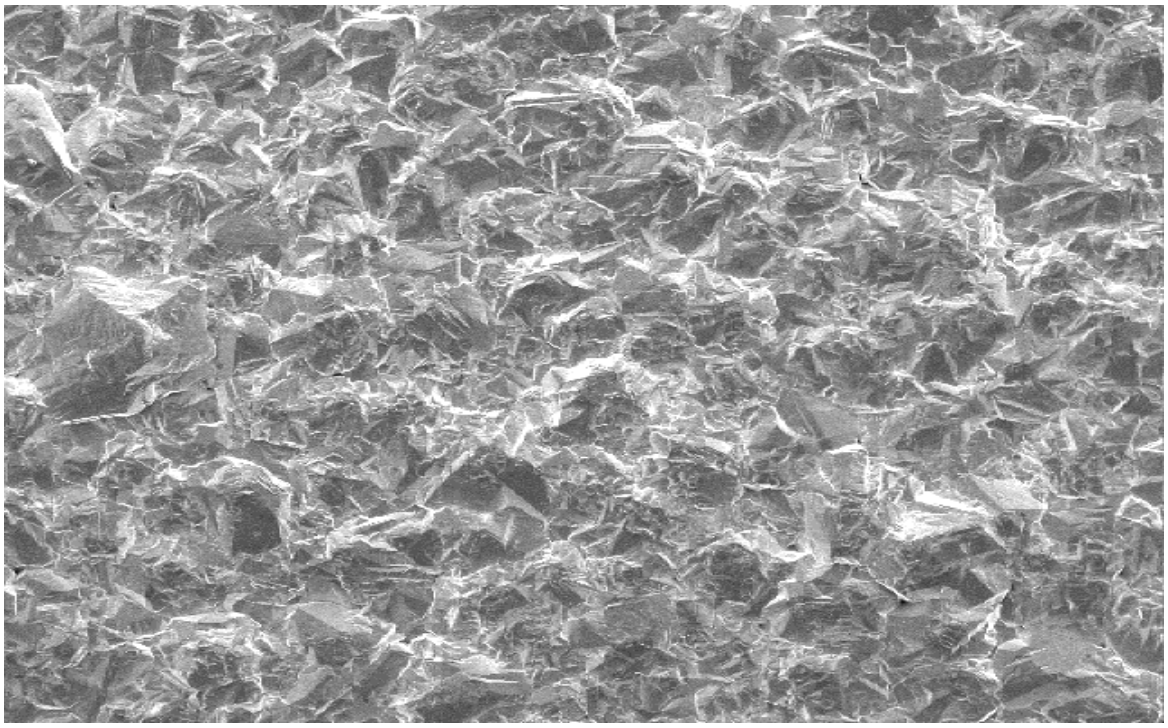

Figure 4-54: SEM Micrograph of the Copper Cathode obtained using APAM after 12 Hours EW time (75X Mag)

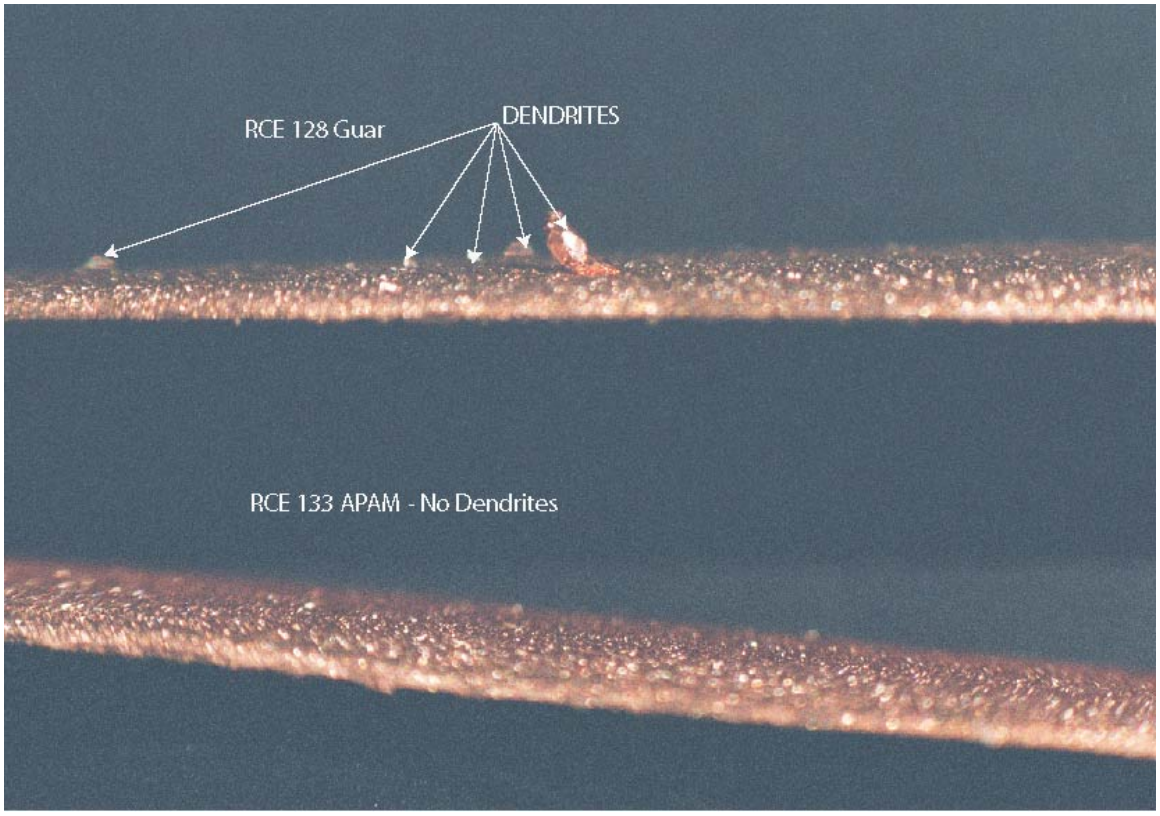

Figure 4-55: Photograph Comparing Guar and APAM after 12 Hours EW Time.

The Copper deposit obtained with Guar shows the presence of dendrites but when APAM was used no dendrites were obtained and its surface roughness was still measurable.

4.4. Discussion and Conclusions

At a 95% confidence interval the model derived from the fractional factorial experimental design in the temperature range of 45-55^{o}C was:

Surface Roughness (μm) =

$$+6.26+0.27*B-0.053*C-0.056*D+0.25*E-0.62*B*C-0.38*B*E$$

The model for the temperature range of 45-65^{o}C was:

Surface Roughness (μm) =

$$+6.16-0.051*A-0.089*B-0.075*C-0.41*D+0.23*E-0.17*B*C$$

where A is temperature; B, current density; C, Guar; D, APAM and E, diffusion layer thickness.

It was deduced that the aliased effect of current density(B)*Guar(C) decreases from significant ($\alpha<0.0001$) in the first model at 45-55^{o}C to insignificant ($\alpha = 0.2120$) in the second model at 45^{o}C-65^{o}C. This reduction in significance is probably due to the faster degradation of Guar at 65^{o}C than at 45^{o}C at the same current density. It can be seen that the effect of APAM is significant in the 45^{o}C-65^{o}C range than in the 45^{o}C-55^{o}C. This significance is probably also due to the faster degradation of APAM at 65^{o}C than at 45^{o}C. This indicates that degraded APAM is more effective at reducing surface roughness than fresh APAM a result which contrasts with that for Guar.

An optimal proportion of Guar to APAM to significantly reduce surface roughness was not determined. Therefore, the role of Guar and APAM was deduced to be independent and therefore Guar and APAM were compared independently as levelling agents.

The evolution of surface roughness/dendrites in copper electrodeposition occurs simultaneously with smaller surface roughness and higher number of PPC where EW time plays an important role as well as the effectiveness of an organic additive, if present, to control the uniformity of the surface profile. In the absence of additives, a

lower surface roughness and a higher PPC was observed than when Guar and/or APAM were present at 30mA/cm^2 and 4.64 hours EW time. This is consistent with AFM studies recently reported [12, 19]. The PPC model for 6-hours EW time indicates that Guar produces higher PPC than APAM. The surface roughness of the copper deposit with Guar was unmeasurable roughness after 12-hours EW time even though 1mg/L Guar was dosed every 3hours (4mg/L Guar total dosage). In contrast, the surface roughness of the copper deposits with APAM was 12.79 and 11.71μm after 12-hours EW time even though a total of 1 and 2mg/L APAM were dosed, respectively. It was therefore shown that the evolution of surface roughness/dendrites up to 12-hours of EW time follows: Nil additives>Guar>APAM.

The results obtained from Tests 3 and 8 in Section 3.4 where polyacrylmide was prepared in water and full-strength electrolyte are similar to the conditions under which Pye and Schurz[17], and Vereecken ad Winand[18] studied nonionic and cationic polyacrylamides and indicated that Guar controlled the surface roughness of electrowon copper more effectively than polyacrylamides. The results of this *Chapter* indicate the opposite of the above publications when PAM was prepared in 16-fold diluted electrolyte at 50^{o}C, for 2-hours under stirring. The preparation of APAM is the major difference between this work and any previous work and it is critical to its levelling effect. APAM is a more effective organic additive to reduce surface roughness than Guar, the industry-standard additive.

4.5 References

1. Paunovic M, Schlesinger M. *Fundamentals of Electrochemical Deposition*: John Wiley & Sons, Inc.; 1998.

2. Schmickler W. *Interfacial Electrochemistry*. New York: Oxford University Press; 1996.

3. Montgomery DC. *Design and Analysis of Experiments*. 5th ed: John Wiley & Sons; 2001.

4. Mahr. *M1 Mahr Perthometer Operating Manual*. 2002.

5. Stat-Ease SME. Design-Expert Software. In. 6.1.10 ed: John Wiley & Sons, Inc; 2003.

6. Arvia AJ, Carrozza JSW. *Mass Transfer in the Electrolysis of Cuso4-H2so4 in Aqueous Solutions under Limiting Current and Forced Convection Employing a Cylindrical Cell with Rotating Electrodes*. Electrochimica Acta 1962;7:65-78.

7. Newman J, Thomas-Alyea KE. *Electrochemical Systems*. Third ed. Hoboken, New Jersey: John Wiley & Sons, Inc.; 2004.

8. MathSoft Engineering & Education I. Mathcad. In. 12 ed; 2004.

9. Grchev T, Cvetkovska M. *Electrochemically Initiated (Co)Polymerization of Acrylamide and Acrylonitrile on a Steel Cathode - Electrochemical and Impedance Study*. Journal of Applied Electrochemistry 1989;19(3):434-42.

10. Grchev T, Cvetkovska M, Stafilov T, Schultze J. *Adsorption of Polyacrylamide on Gold and Iron from Acidic Aqueous Solutions*. Electrochimica Acta 1991;36(8):1315-1323.

11. Grchev T, Cvetkovska M, Schultze JW. *The Electrochemical Testing of Polyacrylic Acid and Its Derivatives as Inhibitors of Corrosion*. Corrosion Science 1991;32(1):103-12.

12. Szymanski G, Dymarska M, Zhao T, Lipkowski J. *Atomic Force Microscopy Study of the Morphology of Electrodeposited Nickel and Copper at Conditions Mimicking Industrial Nickel and Copper Electrorefining*. Electrometallurgy 2001, Proceedings of Annual Hydrometallurgy Meeting, 31st, Toronto, ON, Canada, Aug. 26-29, 2001 2001:375-387.

13. Damajanovic A, Setty THV, Bockris J. *Effect of Crystal Plane on the Mechanism and the Kinetics of Copper Electrocrystallization*. J. Electrochem. Soc. 1966;113(5):429-435.

14. Veilleux B, Lafront A, Ghali E. *Influence of Gelatin on Deposit Morphology During Copper Electrorefining Using Scaled Industrial Cells*. Canadian Metallurgical Quarterly 2002 Jan;41(1):47-61.

15. Kondo K, Murakami H. *Crystal Growth of Electrolytic Cu Foil*. J. Electrochem. Soc. 2004;151(7):C514-C518.

16. Radisic A, West A, Searson P. *Influence of Additives on Nucleation and Growth of Copper on N-Si(111) from Acidic Sulfate Solutions*. Journal of the Electrochemical Society 2002;149(2):C94-C99.

17. Pye D, Schurz G; inventors. The Dow Chemical Company, assignee. Electrowinning of Metals. United States patent 2,798,040. 1957 July 2, 1957.

18. Vereecken J, Winand R. *Influence of Polyacrylamides on the Quality of Copper Deposits from Acidic Copper Sulphate Solutions*. Surface Technology 1976; 4:227-235.

19. Schmidt W, Alkire R, Gewirth A. *Mechanic Study of Copper Deposition onto Gold Surfaces by Scaling and Spectral Analysis of in-Situ Atomic Force Microscopic Images*. J. Electrochem. Soc. 1996(10):3122-3132.