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THE ELECTRODEPOSITION OF ZINC;
CHANGES IN CURRENT EFFICIENCY AND SURFACE STRUCTURE
RESULTING FROM VARIOUS ADDITION AGENTS

BY

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Approved by

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ABSTRACT

An examination of the surface structure of zinc electrodeposited from an acid-sulfate solution was made by scanning electron microscopy techniques. The current efficiencies were also determined, to a lesser extent, in order to correlate the results with the surface structures. Commercial and pure zinc oxide were used to prepare the neutral zinc sulfate solutions. The starting solutions were in a range of acid and zinc concentrations commonly used in commercial practice. Changes in morphology resulting from addition agents such as animal glue, gum arabic, and sodium silicate are compared.

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I. INTRODUCTION

The first patent involving the electrolytic preparation of zinc appeared in 1880.(1) It was not until 1914(2) that the first large scale industrial plant was operating in the United States since the need for pure solution was not recognized initially. Even today there are many basic mechanisms involved in the process that are not fully understood.

The exact flow sheet involved in producing the zinc may vary, but the principal steps involve:

(a) The dissolution of zinc oxide, produced by roasting a zinc sulfide concentrate, in spent electrolyte, to give a neutral zinc sulfate solution.

(b) Purification of the solution to eliminate impurities, harmful to the process, and recovery of these impurities as by-products whenever possible.

(c) Electrolysis of the zinc sulfate-sulfuric acid solution to yield high purity metallic zinc.

The deposition of zinc from an acid solution is possible only because of the high hydrogen overvoltage on zinc. Therefore, any factor which tends to lower the hydrogen overvoltage will cause a decrease in current efficiency or will prohibit zinc from depositing. The primary cause of decreased hydrogen overvoltage is due to the presence of any number of impurity elements, more noble than zinc, which may form local cells on the cathode. This requires either

(a) their elimination to a harmless level in the solution refining process, or

(b) the use of addition agents to compensate for their presence.

The problem is magnified by the fact in many cases extremely minute quantities of impurities, less than 1 mg/ℓ, are sufficient to reduce the current efficiency or sometimes prevent any zinc from depositing. In some instances, the effect of two or more harmful impurities in combination is much more detrimental to the electrolysis than the effect when each of the impurities is present separately. This interaction among impurities, which can possibly work either to impede or assist zinc deposition depending upon the nature and concentration of the species, makes the evaluation of the electrolytic process extremely complex and difficult.

It is well known that the surface structure of the zinc deposit is very important to the overall efficiency of the process. A cathode with smooth surface and a high bulk density is desirable from the standpoint of not only current efficiency but also the melting efficiency. Since the deposit with holes and sprouts has more surface area than that of the uniform dense deposit, a rough deposit will give a large oxidation or drossing loss during the melting operation.

The object of this study was to determine some of the effects that various addition agents and different process conditions have on the surface structure of the zinc deposit. The zinc surfaces were evaluated by means of a scanning electron microscope, which allowed investigation of any deposit regardless of the surface irregularities.

II. LITERATURE REVIEW

There have been many articles published concerning the purification and subsequent electrolysis of zinc sulfate-sulfuric acid solutions. The purifying process used prior to the electrolysis plays an important role in determining the current efficiency and the surface structure of the deposit, however, discussion is limited to the electrolyte and the electrolyzing conditions.

A. Impurities in the Electrolyte. All industrial zinc electrolysis solutions contain a large number of impurities present at many different levels. Even the most rigorous solution purification process will not entirely eliminate the impurities present. For very critical types of impurities, it may not even be possible to detect the impurity chemically, and yet still be detrimental to the process. Therefore, a common definition of a "commercially pure zinc sulfate solution" is a solution which, when used as an electrolyte, will give a good deposit with a high current efficiency.(3)

Probably the most important of all factors associated with zinc electrolysis is the presence of metallic impurities in the deposit. The effect of single impurities has been studied quite extensively and the general effects can be predicted fairly accurately.(3,4) The metallic ions which act as cathodic impurities in the solution may be grouped into four classes according to their effects.

Class 1. Metals whose sulfates decompose at a voltage above that of zinc sulfate. They are sodium, potassium, manganese, aluminum, and magnesium. These elements are regarded as harmless impurities.

Class 2. Metals whose decomposition potential is less than that of zinc, but whose hydrogen overvoltage is higher than that of zinc. They are cadmium and lead, both deposit on the cathode causing impure zinc deposit.

Class 3. Metals whose decomposition potential is higher than that of sulfuric acid, but whose hydrogen overvoltage is less than that of zinc. The common membersof this class are iron, cobalt, and nickel. These metal ions will not deposit with zinc to any appreciable amount but they form local cells in the cathode causing holes or spot burning of the zinc deposit. Their action is probably by alternate deposition and re-solution by the sulfuric acid, since they are soluble in sulfuric acid due to their low hydrogen overvoltage.

Class 4. Metals whose sulfates decompose at a voltage below that of sulfuric acid, and whose hydrogen overvoltage is less than that of zinc. They are copper, arsenic, antimony, germanium, and tellurium. The members of this class, if present in the electrolyte, are deposited with zinc causing points of low hydrogen overvoltage. The impurities which belong to this class are possibly the most injurious to the electrolytic process of zinc.

Sodium, potassium, magnesium, and aluminum. These elements and their compounds are regarded as harmless impurities, if not present in large amounts, in the electrolytic production of zinc. A large amount of these impurities in the solution will reduce the conductivity of the solution and hinder the migration of zinc ions to the cathode. They are also capable of discharging together with zinc and form intermetallic compounds in the zinc deposit.(5)

Manganese. The role of manganese ions, which are added to the solution during the purification process for oxidation purposes, is a rather interesting one. The manganese ions will reduce the corrosion of the lead-silver(1%) anode by the formation of manganese oxide films on the anode surface. Manganous ions are harmful for the cathode process because the highly oxidized manganese ion, MnO_4^-, formed at the anode surface, moves to the cathode by either thermal or bubble agitation and acts as a depolarizer for hydrogen. Manganese oxide suspended in the solution may settle on the cathode surface forming local cells that cause spots of low hydrogen overvoltage. On the other hand, the suspended oxide particles may act as a solution purifier, if they can be precipitated, since they adsorb various impurity elements in the electrolyte.

Cadmium and lead. Cadmium and lead in the electrolyte will deposit with zinc. They are major impurities in the electrolytic zinc. It is known that the presence of small amounts of cadmium and lead in the electrolyte do not drastically lower the current efficiency, however, cadmium and lead must be kept below 50 mg/ℓ and 20 mg/ℓ , respectively, in order to deposit high purity zinc. The solubility of lead sulfate is small in the electrolyte but lead oxides can be formed at the anode surface and migrate to the cathode.

Iron. Iron is normally added to the solution during the purification process in order to co-precipitate arsenic, antimony, and similar impurities and a small amount of iron is always present in the solution. Considerable amounts of iron may be present, up to 20 mg/ℓ, in the electrolyte without noticeable effects on the electrolysis. There is some evidence that the use of iron as an addition agent will reduce the amount of lead in the zinc deposit. The action of iron is probably similar to that of manganous ions which act as an anode depolarizer prohibiting the formation of soluble lead oxides.

Cobalt, nickel, and copper. Cobalt in the electrolyte can be as high as 10 mg/ℓ without causing a serious decrease in the current efficiency. Controlled amounts of cobalt in the solution are beneficial in reducing the amount of lead in the zinc deposit. The exact amount of cobalt that can be tolarated without detrimental effects on the current efficiency is dependent upon the presence of other impurities.

The presence of nickel, as small as 1 mg/ℓ, in the solution will sharply decrease the current efficiency. It causes large holes to be burned in the deposit.

The presence of copper in the solution, more than 10 mg/ℓ,will cause a serious decrease in the current efficiency by lowering the hydrogen overvoltage.

Arsenic and antimony. The presence of arsenic in the solution can be as much as 4 mg/ℓ without causing a serious decrease in the current efficiency if no other impurities, harmful to the process, are present.

Antimony in the solution is very detrimental to the cathodic zinc process. The current efficiency is drastically decreased by the presence of antimony, in concentrations as low as 0.02 mg/ℓ, due to the re-solution of the deposit.

Germanium, selenium, and tellurium. Their presence in the solution is perhaps the most detrimental to the zinc electrolysis. The presence of these impurities, 0.01 mg/l or less, may cause a sharp decrease in the current efficiency due to serious re-solution of the deposit. Germanium, antimony, and arsenic are also known to deposit on zinc in the form of alloys and they form volatile hydrides with hydrogen thus setting up local galvanic cells.

Thallium and tin. The current efficiency is not affected by the presence of small amountsof thallium in the electrolyte. Thallium will deposit with zinc and contaminate the zinc deposit.

The presence of small amounts of tin in the solution will decrease the current efficiency. One characteristic of a deposit made from a solution containing tin is the shiny deposit which results even when the concentration of tin is small enough to cause no decrease in the current efficiency.

Bismuth, tungsten, indium, and gallium. These elements are not likely to be found in the electrolyte as they are easily removed in the solution purification process.

Silver. Small amounts of silver are always present in the electrolyte due to the corrosion of the lead-silver(1%) anode. The solubility of silver in the electrolyte, however, is small due to the formation of an insoluble silver sulfate. It is known that silver will deposit with zinc and contaminates the deposit. There was no publication available as to the exact role of silver in the cathodic process of zinc.

Halogen ions. Chlorine and fluorine ions are commonly found in the electrolyte and their presence is undesirable.

Cl^- increases the corrosion of the lead anode. The presence of permanganate, formed at the anode surface, tempers the effect of Cl^- by oxidation of Cl^- to Cl_2 before Cl^- reaches to the anode.

The presence of small amounts of fluorine, 2 mg/l, in the solution causes the zinc deposit to stick on the aluminum starting sheet and sometimes it is impossible to remove the deposit. The sticking is due to the removal of thin protective aluminum oxide films by their reaction with fluorine.

Impurities in combination. Zelezny et al.(6) and Turomshina et al.(7) have studied the effect of combinations of impurities in the electrolyte. These works were usually limited to two species in combination since the presence of more than two elements makes the study so complex. Figs. 1 and 2 show examples of the combined effects of antimony with germanium and arsenic with germanium, respectively, on the current effciency.

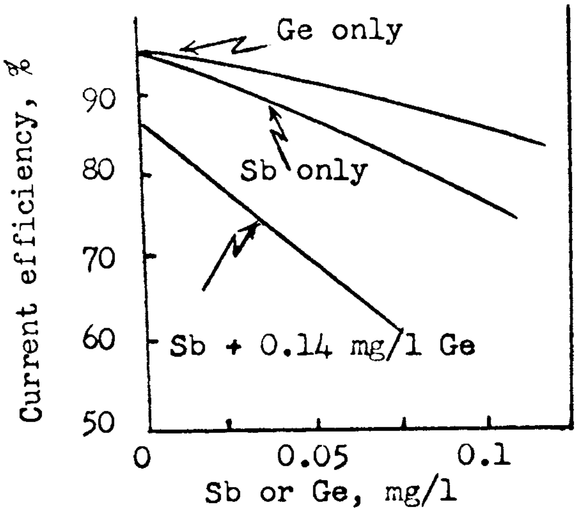

Fig. 1 - The combined effect of antimony and germanium.(6)

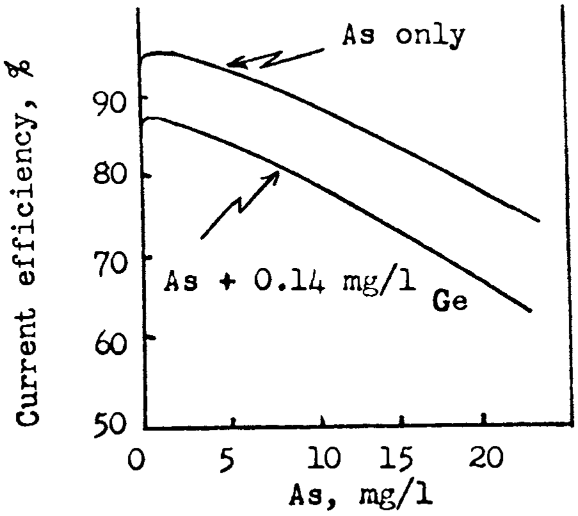

Fig. 2 - The combined effect of arsenic and germanium.(6)

The entire problem is further complicated if some addition agents are added to the electrolyte. The additions of small amounts of gum arabic, gum tragacanth, manganese, and dichromate tend to temper the detrimental effect of germanium.

B. Addition Agents. Colloidal organic addition agents such as glue and gum arabic are often used to increase the overall efficiency of the electrolytic zinc process. If proper amounts of these addition agents are used, they are beneficial in increasing the current efficiency and improving the physical characteristics of the zinc deposit. The additives may work as surface active agents or as a coagulant for harmful colloidal impurities which are suspended in the solution. For this reason the effect of the additives on the cathodic process can not be discussed separately from that of impurities in the electrolyte. The addition agents may assist the zinc deposition for a certain solution with particular impurities, while the same additives may increase the detrimental effects of the impurities for a solution with some other impurities. There have been numerous articles published concerning the effect of various additives on the current efficiency ever since the beginning of the zinc electrolysis. This type of investigation is extremely difficult for the reason mentioned above. Moreover, the presence of permanganate ions and manganese oxide, both produced during the electrolysis, make the study very difficult since these manganese compounds react with the organic additives to some extent. For example, it is known that the adhesion of manganese oxide films to the anode is better with a glue addition. This indicates the reaction of the organic additives can be extended not only to the cathode surface but also to the anode surface as well.

Inorganic addition agents have a very limited use. Silicates of sodium and potassium, carbonates or hydroxides of barium and strontium are often added to the solution either to improve the surface characteristics or to decrease impurity concentrations in the zinc deposit. Barium and strontium compounds are added mainly to decrease the lead content in the deposit.

C. Cell Temperature. Increase in the cell temperature increases the rate of re-solution of the zinc cathode thus decreasing the current efficiency. The efficiency is much less affected by temperature if the solution is sufficiently pure. The current efficiency decreases rapidly as the temperature of the solution increases if the solution contains germanium, arsenic, antimony, nickel, cobalt, and similar impurities. Rise in temperature increases the conductivity of the solution but lowers the hydrogen overvoltage and the net result is the decreased current efficiency.

D. Current Density. In general, the current efficiency increases with increase in the current density, however, the effect may be reversed if harmful impurities are present, depending upon the nature of the species. Less than 40 ampere per square foot, asf, is considered to be a low current density process while more than 80 asf is referred to as a high density process.

E. Crystallographic Aspects of Zinc Deposit. There are not many articles published concerning studies of the surface morphology of zinc deposits by electron microscopy or scanning electron microscopy techniques. Sato(8) and Naybour(9) have studied the surface structure of the electrolytic zinc deposit. Sato has examined the surface of the electrolytic zinc from zinc sulfate-sulfuric acid solutions by both electron microscopy and electron diffraction techniques to determine the effect of organic addition agents on the crystal orientation. The work has been limited to short time deposits, however, because the replication of the surface became difficult for long hour deposits due to the increase in surface roughness. These deposits were made from solutions containing no manganese ions and a platinum anode and a brass cathode. These conditions are drastically different from normal practice, so that it can only be speculated as to whether these results are true using different plating procedures.

In general, a $(11\cdot\ell)$ orientation was characteristic of the electrolytic zinc from zinc sulfate-sulfuric acid solutions without any additives. With small amounts of organic additives in the solution, the surface layer of the zinc deposit became flat as a result of increased cathode polarization and hence throwing power of the electrolyte. Pretein or carbohydrate additions to the solution, roughly 50 mg/ℓ, made the surface irregular, and 10 mg/ℓ or less of gum arabic additions made the surface inhomogeneous and decreased the current efficiency greatly. As the amount of these additives, except gum arabic, increased the orientation changed from $(11\cdot\ell)$, $\ell\sim 4$, $\rightarrow(10\cdot\ell)$, $\ell\sim 1$, $\rightarrow(11\cdot 2)$ to $(11\cdot 0)$. With gum arabic additions the $(10\cdot\ell)$, $\ell\sim 1$, orientation was not observed and the orientation changed from $(11\cdot\ell)$, $\ell\sim 4$, directly to $(11\cdot 2)$ $(11\cdot 0)$.

III. EXPERIMENTAL

The experimental section is presented in two parts, preliminary experiments and experimental materials and apparatus.

A. Preliminary Experiments. In order to aquaint the author with the zinc electrolysis numerous short time electrodepositions were tried. Various physical arrangements were used in this portion of the study before arriving at the best set of conditions, which were then used throughout the remainder of the work. These are described fully in the next section.

Three kinds of cells, made of corroding grade lead, lead-antimony(6%) alloy whose inside walls were coated with the Glyptol paint, and a glass beaker with a modified pouring spout were investigated. The lead-antimony cell was inadequate due to the cracking of the coated film after using it for a few days. The cell acid penetrated these cracks and corroded the alloy, thus contaminating the electrolyte with antimony, which is one of the most harmful impurities in the electrolytic zinc process. The glass cell gave the most consistent results among the three.

The anode was made from corroding grade lead. There was a sharp increase in the current efficiency when the lead anode was replaced by lead-silver(1%) alloy. This was thought to be a result of the greater corrosion resistance of the alloy. Three kinds of starting cathode, which were made from sheets of aluminum, zinc, and electrolytic copper, were compared. The copper was unsatisfactory because it caused lower current efficiencies. The zinc and aluminum wer both satisfactory for short hour runs but the zinc deteriorated during long runs at the solution level. Thus because it behaved well under most all conditions and since it is used in commercial practice, aluminum was chosen for the starting cathode material.

Initially, C. P. grade sulfuric acid and zinc sulfate were used to make the electrolytes. The concentrations of zinc and acid were from 5 to 130 grams per liter, gpl, and from 25 to 150 gpl, respectively. No manganese was added to the electrolyte. The current densities were varied from 5 to 120 asf depending upon the concentrations of zinc and acid. Usually a higher current efficiency resulted with a higher current density, however, these results were very difficult to evaluate and lacked consistency. All these cathode surfaces were rough and honeycombed regardless of the concentrations of zinc and acid or the change in the current density. The need for a purer solution and the lead silver anode was apparent.

Additional starting solutions were made using an industrial purified neutral zinc sulfate solution($\sim$170 gpl Zn^{++} and $\sim$3.5 gpl Mn^{++}) and C. P. grade sulfuric acid. The concentrations of acid and zinc were varied from 100 to 225 gpl and from 30 to 150 gpl, respectively. A glass cell was used with one aluminum starting cathode between two lead-silver(1%) anodes. Generally, the current efficiencies were 85 to 90 % with concentrations of 200 gpl or less sulfuric acid and 50 gpl or more zinc. The deposit always had a rough and honeycombed surface regardless of the concentrations of acid and zinc.
Various addition agents were added to the electrolyte, indivi-

dually or in combinations, in varying amounts in an attempt to make a dense uniform deposit without holes. The results indicated that the use of sodium silicate with animal glue or gum arabic was necessary to make the surface uniform and smooth. Further investigations indicated that the use of C. P. grade sulfuric acid with the neutral zinc sulfate solution could not produce the deposit without holes even though the current efficiency was above 90 %.

The acid concentration of the third type of the starting solution was built up from the zinc dust re-refined neutral zinc sulfate solution by depositing zinc from the solution. Additions of sodium silicate with animal glue and/or gum arabic in combination to the starting solutions produced a very dense uniform deposit witha smooth surface.

It was found that the anode surface must be covered with enough manganese oxide film(pre-conditioning) to make the deposit dense with a uniform surface. During the acid build up, a gradual change in color of the electrolyte, from yellow to purple, was observed as the electrolysis progressed. This indicated the gradual formation of the low oxide(Mn_3O_4, Mn_2O_3) to the higher oxide(MnO_4^-) as the acidity increased. When the cell reached the equilibrium state, there were appreciable amounts of MnO_2 suspensions with small amounts of MnO_4^-, less than 0.1 gpl. Some of the manganese present in the solution was oxidized and manganese oxide scales fromed on the anode surface during the electrolysis, while some of the oxide particles formed were suspended in the solution. Spectrophotometric analysis showed that these particles contained magnesium, calcium, zinc, and manganese as major constituents and traces of lead, cobalt, silver, nickel, copper, tin, aluminum, and silicon.

B. Experimental Apparatus and Materials. The experimental apparatus and materials section is presented in six parts: electrolyzing cell, anode, cathode, electrical equipment, feed pump, and electrolyte.

1. Electrolyzing cell. The electrolyzing cells were made from one-liter glass beakers whose pouring spouts were modified in order to accomodate the withdrawal of the constant overflow.

2. Anode. The anode, 1½ in. x 4½ in., was made from a 1/8 in. thick sheet of a lead-silver(1%) alloy with square holes, 3/8 in. x ½ in., which covered approximately 50 % of the surface area. These holes were punched to assist not only the adherence of the manganese oxide films but also the movement of the electrolyte around the anode.

In all cases the anode was pre-conditioned in the similar electrolyte used for the experiment for more than 24 hours prior to the test. The pre-conditioning of the anode is an important step in electrolyzing zinc, but is not completely understood. Basically the process involves depositing a proper film of manganese oxide on the lead. When sufficiently conditioned, the further oxidation of lead to Pb^{+2} and thus diffusion into the solution is retarded. This seems to improve both the current efficiency and physical and chemical properties of the deposit. There are probably a series of complex reactions with many different phases being formed during the conditioning cycle. X-ray diffraction patterns of the manganese oxide scale indicated that the structure was amorphous.

3. Cathode. The cathode, 1 1/8 in. x 4 in., was made from 1/32 in. thick low alloy aluminum sheet. One cathode was placed between the two anodes in each cell making the spacing approximately $1\frac{1}{2}$ in. from anode to cathode.

Plexiglas edge strips were placed on both edges of all cathodes to eliminate the edge sprouting.

4. Electrical equipment. A constant power supply, QRC-40-15, made by Sorenson Company was used throughout the experiments. This unit was operated in constant current mode. The current efficiencies were measured using an ampere-minute meter which was purchased from Sangamo Electric Company. The cell voltage was monitored on a D. C. digital voltmeter, C-211, made by United Systems Corporation. The electrolyte temperature was first controlled by placing the cells on a hot plate but later they were kept in a water bath for better control of temperature.

5. Feed pump. The constant additions of the neutral zinc sulfate solution and the additives(1 to 10 mg/ml water solution) to the cell were made by the Vibrostaltic pumps, made by Chemical Rubber Company. However, it was rather difficult to control small flow rates. Later all additives were mixed with the neutral zinc sulfate solution and the mixture was fed into the cell by one Vibrostaltic pump. The Vibrostaltic pump was later replaced by a Microbellows pump, made by Research Appliance Company, for the better control of the flow. The overall experimental set up is shown in Figure 3.

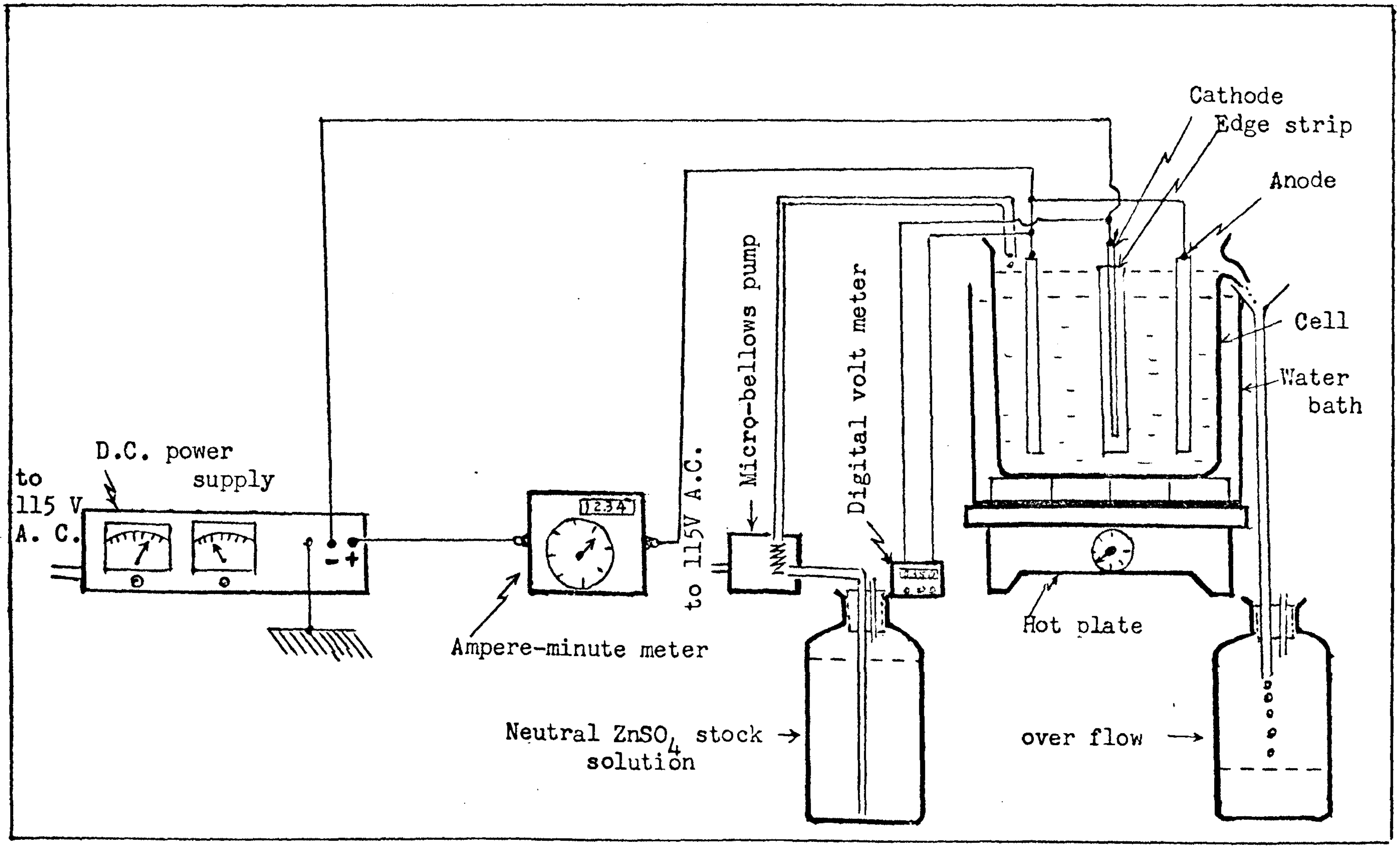

Fig. 3 - Sketch of the experimental apparatus.

6. Electrolyte. There were two types of solutions used in this work. One was an industrial neutral zinc sulfate solution produced by the leaching of zinc oxide, obtained from roasting a zinc concentrate, with subsequent regular solution purification. This solution was filtered first and was re-refined with zinc dust by heating to near the boiling point for 30 minutes. This solution was filtered while still hot to remove residual zinc dust.

The acid concentration was built up in the cell by depositing zinc from the refined neutral solution. This was done in order to keep the impurity content as low as possible and to eliminate possible extraneous results due to the introduction of impurities from C. P. grade sulfuric acid if it was used.

The second type solution was made using enough pure zinc oxide (99.95 %) dissolved in C. P. grade sulfuric acid to give a neutral solution. Manganous sulfate was added to the acid solution prior to the dissolution of the zinc oxide to give 3.0 gpl Mn^{++}in the final solution. A small amout of $KMnO_4$($\sim$3 ml/l of N/10) was also added for oxidation purposes while the solution was acidic. Water was then added to adjust the concentration after the solution reached the neutral point. This solution was heated to near boiling to make the precipitation complete and filtered, then zinc dust treatment and filtering, identical with that for the commercial electrolyte, was completed.

The electrolyte composition was held in the range $\sim$200 gpl H_2SO_4, $\sim$65 gpl Zn^{++} and $\sim$2.5 gpl Mn^{++} initially, for all experiments, except where the effect of one of these was to be determined.

IV. RESULTS AND DISCUSSION

The main portion of this study involved the determination of the effect on surface structure of the electrodeposited zinc resulting from certain additives to the electrolyte, and to a lesser extent, the range of current efficiencies that results when the additives are used. A limited examination of the effect of acid and zinc concentrations was also carried out. The surfaces were investigated using a scanning electron microscope.

A. Commercial Electrolyte. A summary of the results of the experiments conducted using commercial electrolytes under varying conditions is shown in Table 1 and 2. When "no additives" is given as the condition, it is meant that no additional additives are used but the solution may already contain some residual additives. There should only be very small quantities of these additives remaining, since most of the residual additives are believed to be removed during the solution purification processes at the plant. Also a number of runs were made above 65 asf, up to 120 asf, and for the most part higher current density gave better current efficiencies and structure than those obtained using lower current density.

The electrolyte composition was changed in the range 150 gpl sulfuric acid and 85 gpl Zn^{++} to 225 gpl acid and 35 gpl Zn^{++}. Figures 4 to 7 show the structures resulting from variations in acid concentration. For the higher acid concentration the structure was more open and rougher than that the lower acid concentration and a

Table 1. - Effect of H_2SO_4 and Zn^{++} Concentrations.[1]

H_2SO_4, gpl	Zn^{++}, gpl	Run-No	Time, min.	Cell Voltage, volt.	C. Eff., %
~150	~85	95-1	35	3.10 to 3.20	93.6
		-2	60		95.0
		-3	120		96.0
		-4	240		94.0
		-5	480		93.8
~ 175	~ 65	93-1	35	3.07 to 3.18	95.6
		-2	60		94.0
		-3	120		94.5
		-4	240		95.8
		-5	480		84.2 *
~ 200	~50	96-1	35	3.05 to 3.13	90.0
		-2	60		91.5
		-3	120		92.0
		-4	240		90.8
		-5	480		82.5 *
~ 225	~35	97-1	30	3.03 to 3.05	84.2 *
		-2	60		88.0 *
		-3	120		78.7 *
~ 175	~65	99-1	120	3.46	95.0 (25°C)
		-3	120	3.04	79.7 *(65°C)
~ 200	~ 50	100-1	120	3.42	93.2 (25°C)
		-3	120	3.04	88.5 * (65°C)

1. Commercial Electrolyte; ~2.5 gpl Mn^{++} Cell temp.; 45±3°C, C. Density; 65 asf, No additives used.

* Severe re-solution.

Table 2. - Effect of Addition Agents.[1]

Additives, mg/g Zn deposited		Run-No	Cell Voltage, volt.	C. Eff., %
Animal glue	0.01	101-1	3.18 to 3.20	88.0
	0.10	-2		87.0
	1.00	-3		93.0
Gum arabic	0.01	103-3	3.09 to 3.14	95.2
	0.05	-1		96.0
	0.10	-2		88.5
Sodium silicate	0.10	102-1	3.13 to 3.14	88.5
	1.00	-2		91.1
	10.00	-3		91.5
0.50 mg/g of sodium silicate + Animal glue	0.10	104-1	3.15 to 3.18	90.0
	0.20	-2		91.7
	0.40	-3		93.3
	0.60	-4		93.5
	0.80	-5		93.0
	1.00	-6		92.4

1. Commercial Electrolyte; ~200 gpl H_2SO_4, ~65 gpl Zn^{++}, ~2.5 gpl Mn^{++}, Time; 2 hours, Current density; 65 asf, Cell temperature; 45 ± 3°C.

pronounced decrease in the current efficiency was also noted. A heavy honeycomb-like film is very much in evidence at 3,000 X particularly with high acid concentration. X-ray and electron microprobe analyses failed to reveal any phase other than zinc.

Figs. 8 through 13 show the effect of temperature on the surface structure. At 25°C the presence of some preferred orientation is evident, however, the film appears in the area surrounding the protrusions. The surface structure became rather open and irregular as the temperature of the cell increased.

Figs. 14 to 16 show the effect of animal glue concentration on the surface structure. The decrease in grain size and increase in apparent bulk density is evident as the animal glue concentration is increased. No film is observed in Fig. 15 while Figs. 14 and 16 have some films, however, Fig. 16 has much less than Fig. 14. The absence of a film for the glue concentration approximately 0.1 mg/g, (0.1 mg of glue per gram of zinc deposited), was observed in various other experiments.

With small amounts of glue, the hydrogen bubbles were quite large and tended to adhere to the electrode. The bubble size and sticking both decreased with increased glue concentrations. In general, when hydrogen gas would adhere to the cathode, the surface was relatively rough and cratered, and gave a rather open irregular structure.

Sodium silicate additions produced structures as shown in Figs. 17 to 19. There was no notable change in the structure as the amount of sodium silicate additions was varied. Addition of 1 mg/g of sodium silicate means that 1 mg of a 35 % sodium silicate, ($Na_2O:SiO_2$ $=1:2.5$), in water solution is added per gram of zinc deposited.

There is a distinctive change in the structure with variations in the amount of gum araoic as shown in Figs. 20 to 22. Small amounts of gum arabic additions were sufficient to produce a very distinctive orientation(basal plane parallel to the electrode surface). Increasing the amounts of the addition agent gave a rougher, more open structure, without the plate-type deposit. The high concentrations also produced a very dark colored deposit with very low current efficiency. Small amounts of gum arabic additions caused a slight frothing of the cell while the additions of more than 0.1 mg/g produced no notable frothing. The cathode was very brittle with the addition of 0.1 mg/g of gum arabic.

Figs. 23 through 27 show the variations of surface structure using combinations of sodium silicate and animal glue. It is clear that the combination of the two additives tends to produce a dense plate-type structure in the range of 0.1 to 0.4 mg/g of animal glue additions. X-ray examination of these materials correlated well with visual observations as a considerable amount of basal plane preferred orientation was shown. The crystal size became more random and smaller with increasing glue concentrations. Figs. 28 and 29 show a distinctive change in the orientation in some areas as the glue concentrations increased above 0.6 mg/g. Fig. 30 shows a top of the fin-like structure at a higher magnification.

B. <u>Electrolyte made from Pure Zinc Oxide</u>. A summary of the results of the experimentsusing pure ZnO is given in Table 3.

Table 3. - Effect of Addition Agents.[1]

Additives, mg/g Zn deposited		Run-No	C. Voltage, volt	C. Eff., %
No additives		107-3	3.26 to 3.29	93.4
		-4		93.8
Animal glue	0.01	111-1	3.23 to 3.26	92.6
	0.10	-2		89.5
	1.00	-3		85.2
Gum arabic	0.01	112-1	3.21 to 3.27	93.2
	0.05	-2		91.7
	1.00	-3		90.0
Sodium silicate	0.10	114-1	3.21 to 3.25	92.5
	1.00	-2		91.5
	5.00	-3		90.3
2 mg/g of sodium silicate + 0.5 mg/g animal glue	(23 hours)	106-2	3.22 to 3.45	95.5
	(18 hours)	-3		95.0
	(4 hours)	-5		91.7

1. Pure ZnO Electrolyte: ~200 gpl H_2SO_4, ~65 gpl Zn^{++};
~2.5 gpl Mn^{++} Time; 2 hours, Cell temperature; 45±3°C
Current density; 65 asf.

The surface structures of the zinc deposit resulting from the electrolyte without any additives are shown in Figs. 31 and 32.

The effect of a high Mn^{++} concentrations without any additives on the surface structures are shown in Figs. 33 and 34. It is evident that the amount of honeycomb-like film increases with increasing manganese concentrations. It appears that the current efficiency decreases with increasing amounts of the film. The apparent surface area increases as the amount of film increases and lowers the current density. For this reason the amount of the film may be controlled by the current density since low current density tends to produce more film than the higher current density.

Figs. 35 to 38 show the results produced by varying the glue concentrations. A notable change in the structure to a fin-type structure, protruding from the surface, is evident as the glue concentration increased. With increasing glue concentrations, the orientation appears to change 90 degrees from the basal plane parallel to the electrode surface.

Figs. 39 to 42 show the effect of gum arabic additions on the surface structure. Gum arabic additions produced structures quite different from those seen on the previous electrodes made from the industrial electrolyte. There was also a tendency for the surface to appear rougher with a very fine nodular-type growth in evidence. Also there was no evidence of brittleness with this electrolyte. There was a tendency toward a plate-type structure, but in general, the deposits were more massive and without particularly sharp detail.

No distinctive surface variation was seen when the amount of sodium silicate additions was varied as it was with the commercial electrolyte. An example of this is shown in Figs. 43 and 44. The number of holes in the cathode surface decreased with increasing amounts of sodium silicate, thus the overall surface was rather flat at higher silicate additions.

The fin-type structure produced from a combination of sodium silicate and animal glue additions is shown in Figs. 45 and 46. An unknown impurity, possibly manganese oxide, is seen adhering to the electrode surface. The structure surrounding the particle is identical with the plate-type structure which is shown previously with the commercial electrolyte, but the majority of the structure is of a continuous fin-type deposit.

The film was easily produced by changing one of the depositing parameters from normal conditions(~ 200 gpl H_2SO_4, ~ 65 gpl Zn^{++}, and 45°C) to a high acidity(250 gpl), a very low current density(5 asf), and a high cell temperature(65°C). All these conditions produced the film to some extent. Some of the examples are shown in Figs. 47 and 48.

C. <u>Commercial Deposits.</u> In order to acertain whether there was some degree of applicability of the laboratory results to commercial practice, the structure of a number of industrial deposits was also checked. Samples cut from 2, 6, 8, 12, and 24 hour deposits are shown in Figs. 49 through 53. The film started to appear after 6 hours of depositing time and the number and the size increased with increasing deposition.

V. CONCLUSIONS

The surface structure of the electrodeposited zinc is greatly affected by the nature and amount of additives to the electrolyte.

The variations in the amount of sodium silicate additions did not change the microstructure of the surface nor the current efficiency drastically, however, the overall surface was rather smooth with addition of more than 5 mg/g.

The addition of animal glue between 0.1 and 0.5 mg/g produced a dense plate-type structure, while the use of more than 0.5 mg/g made the surface rough with a protruding fin-like structure in some areas.

The variations in the surface structure were drastic for commercial electrolyte when the amount of gum arabic additions were varied. As little as 0.01 mg/g of gum arabic additions produced a plate-type dense deposit. The surface structure was completely changed when 0.10 mg/g of the additive was used. The deposit was very dark and brittle with a very poor current efficiency.

Better deposits were usually obtained by using combinations of addition agents. The concentration of the addition agents required in the combination could be estimated, however, by noting the changes produced by the additives when checked individually. Insufficient or excess quantities were frequently indicated by lower current efficiencies, or by poor structural characteristics such as pin holes, surface roughening, or protrusions.

There seemed to be a trend occurring on deterioration of the deposit with time. If the long time deposit was not considered to be very good, this could often be indicated earlier in the deposit cycle by the presence of certain of the surface characteristics which were mentioned earlier. For a very good deposit, the structure remained much more uniform with respect to elapsed time.

In general, it appears that variations in deposition behavior can be followed by surface examination at high magnification, using a scanning electron microscope.

VI. RECOMMENDATIONS

In the interest of further research into the electrowinning of zinc from acid-zinc sulfate solutions, a few suggestions are made.

A. Anode Reaction. It would be very beneficial to investigate the precise nature of the anode reaction with not only manganese and its compounds present in solution but also with colloidal impurities in the solution. An investigation of the effect of the organic additives on the anode should be also included.

The behavior of silver in the anode, physically, chemically, and electrochemically should be studied, particularly from the standpoint of reactivity with impurities and additives in the solution.

B. Cathode Reaction. Studies on colloidal effects on the cathode deposit should be made, similar to those mentioned above for the anode. The nature of the study might be quite different however due to the continuous change of the cathode due to depositing zinc.

The variation in the structure of the deposit and the current efficiency as a function of the impurity or combinations of impurities should also be investigated. Of particular interest would be the behavior of silver, since there does not seem to be any information in the literature regarding this element.

C. Colloid Particles. Some study of colloidal impurities and/or additives which are suspended in the electrolyte should be made, because of the substantial and varied effects these reagents have on the morphology and efficiency of the deposit. It may be possible to use some sort of diaphram around both anode and cathode to study the nature of these suspensoids.

D. Miscellaneous. A brief study on such variables as current density and temperature under closely controlled conditions, possibly using an inert anode such as platinum orcarbon, might be warranted. The surface morphology obtained in these experiments might prove very informative.

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VIII. VITA

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APPENDIX A

Preparation Of Zinc Sulfate Solution From Pure ZnO

The following is the flow sheet for the preparation and purification of the neutral zinc sulfate solution from pure zinc oxide.

For 4,000 ml. of zinc sulfate solution containing ~200 gpl Zn^{++} and ~3 gpl Mn^{++}

1. Measure approximately 2,500 ml. of distilled water into a 4 liter beaker.
2. Add 660 to 680 ml. of C. P. grade sulfuric acid.
3. Add 120 ml. of C. P. grade manganese sulfate solution containing 0.1 g/ml. Mn^{++}
4. Add 2 to 3 ml. of N/10 $KMnO_4$ solution.
5. Weigh approximately 1,000 grams of pure zinc oxide and make a paste with water.
6. Add pure zinc oxide paste to the acid until the neutral point(methyl orange to yellow).
7. Heat to near the boiling point to complete the coagulation and precipitation.
8. Filter through # 41 Whatman paper or filter pulp depending upon the size of the precipitate.
9. Add 10 grams of zinc dust to the filtrate.
10. Heat to near the boiling point for at least 30 minutes.
11. Filter through # 41 Whatman paper to remove excess zinc dust.
12. Adjust the volume to 4,000 ml.

APPENDIX B

Purification Of Commercial Neutral Zinc Sulfate Solution

The following is the flow sheet for the purification of the commercial neutral zinc sulfate solution which contains $\sim$170 gpl Zn^{++} and $\sim$3.5 gpl Mn^{++}

1. Pour the neutral solution into a 4 liter beaker.

2. Heat to near the boiling point.

3. Add 3 to 5 ml. of N/10 $KMnO_4$ or until the solution becomes yellow.

4. Filter through # 41 Whatman paper or filter pulp depending upon the size of the precipitate.

5. Add 20 grams of zinc dust.

6. Heat to near the boiling point for at least 30 minutes.

7. Filter through # 41 Whatman paper to remove the excess zinc dust.

8. Adjust the volume to the original to compensate the evaporation.

APPENDIX C

Acid Build-Up From Neutral Zinc Sulfate Solution

The following is the flow sheet for the acid build-up from both the commercial and pure zinc oxide neutral zinc sulfate solutions.

1. Pour the neutral zinc sulfate solution into 1 liter beaker -cell.

2. Secure the electrodes in place.

3. Turn on the power supply and set to obtain a current density of 30 asf for 2 to 3 hours, then increase the current density to 45 asf for 40 hours. Use 65 to 70 asf for at least one hour before turning off the power supply.

4. Remove all electrodes when the acidity is built up to ~250 gpl.

5. Filter through filter pulp to remove any precipitate from the solution. (Examples of the composition of the precipitates are shown in the Table 4 below)

6. Adjust the acidity to the desired level by adding the neutral stock solution.

Table 4 - Spectrophotometric Analyses of the Precipitates.

N. Solution	Ag	Al	Ca	Cu	Ni	Fe	Co	Mg	Mn	Pb	Si	Sn	Zn
Commercial	T	T	M	T	(t)	T	(t)	P	P	T	T	T	P
Pure ZnO	T	T	-	-	-	T	-	-	P	T	T	-	P

P: predominant, M: minor, T: trace, (t): sometimes trace amount.

APPENDIX D

Scanning Electron Micrographs

Some of the surface structures examined under a scanning electron microscope are shown in Figures 4 through 53.

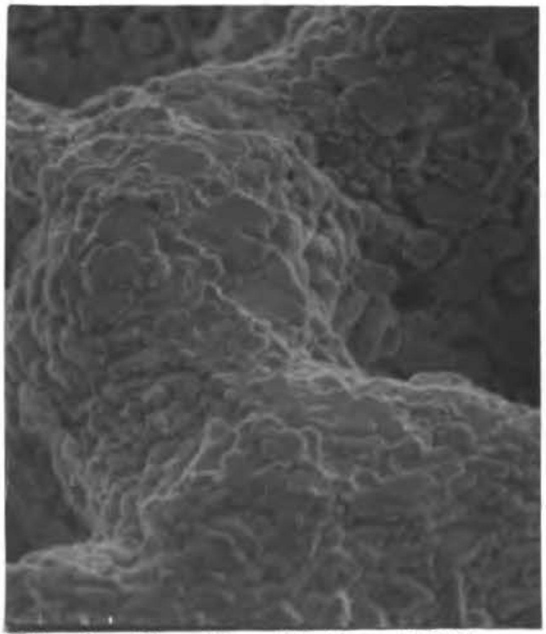

Fig.4 – Run-No 95-3, 300X

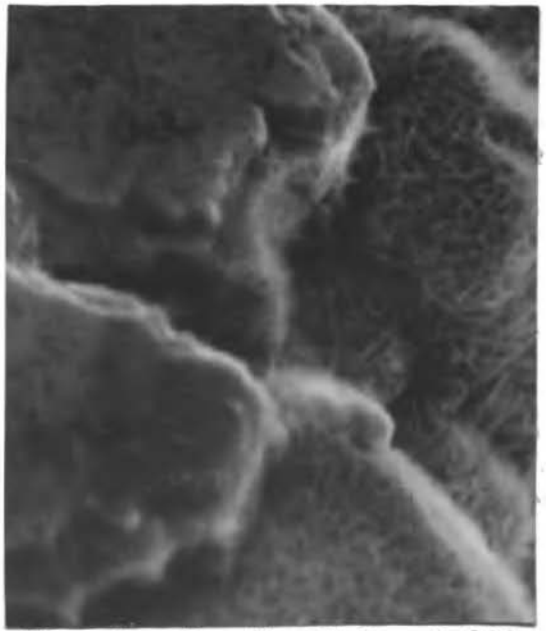

Fig. 5 – Run-No 95-3, 3,000X

Commercial Electrolyte: ~150 gpl H_2SO_4, ~85 gpl Zn^{++}, ~2.5 gpl Mn^{++},
No additives, C. density; 65 asf, C. temp.; 45°C, 2 hour deposit.

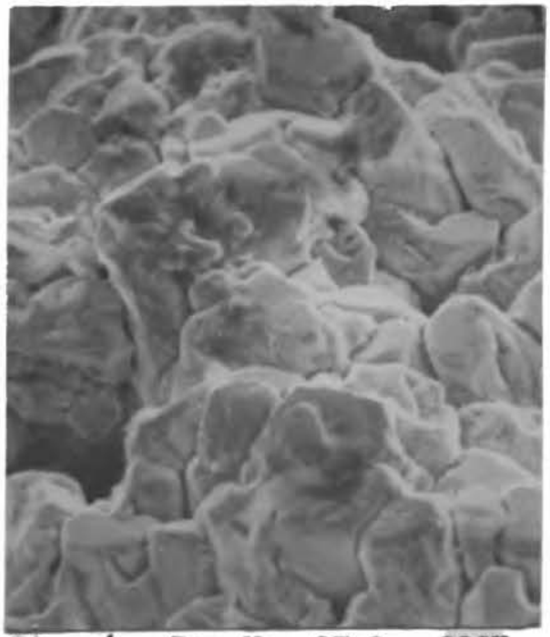

Fig. 6 – Run-No 97-3, 300X

Fig. 7 – Run-No 97-3, 3,000X

Commercial Electrolyte: ~225 gpl H_2SO_4, ~35 gpl Zn^{++}, ~2.5 gpl Mn^{++},
No additives, C. density; 65 asf, C. temp.; 45°C, 2 hour deposit.

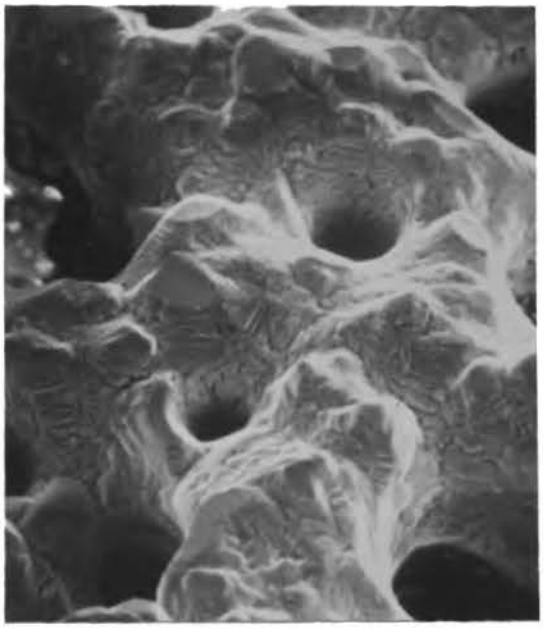

Fig. 8 - Run-No 100-1, 300X

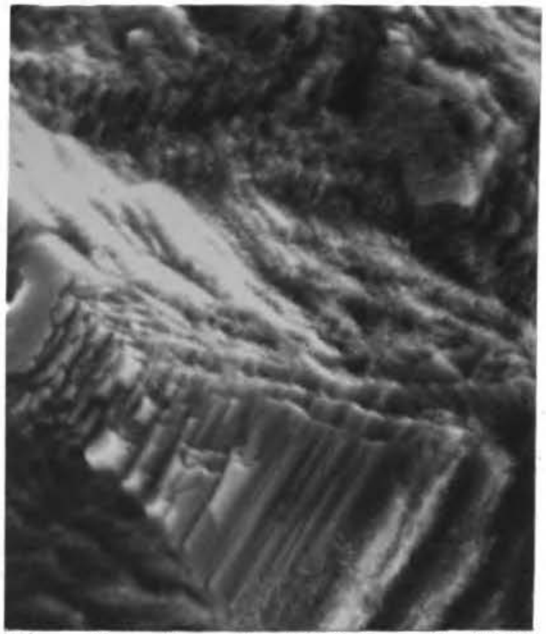

Fig. 9 - Run-No 100-1, 3,000X

Commercial Electrolyte: $\sim$200 gpl H_2SO_4, $\sim$50 gpl Zn^{++}, $\sim$2.5 gpl Mn^{++}
No additives, C. density; 65 asf, C. temp.; 25°C, 2 hour deposit.

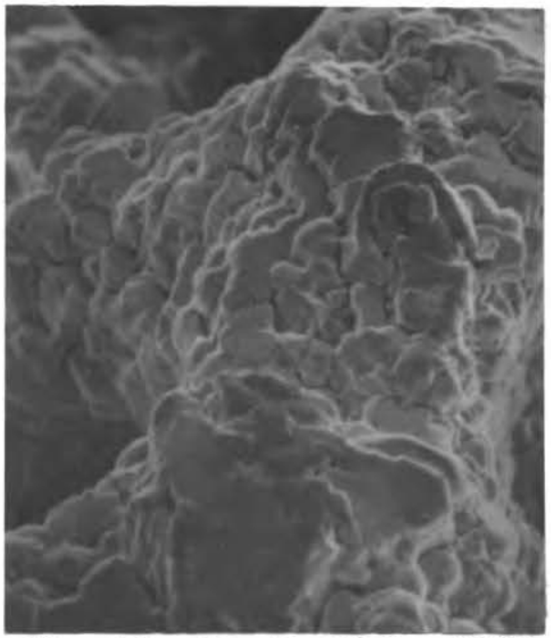

Fig. 10 - Run-No 96-3, 300X

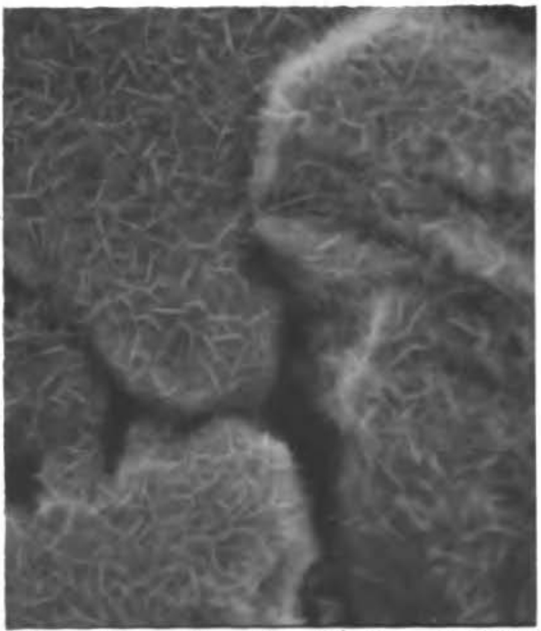

Fig. 11 - Run-No 96-3, 3,000X

Commercial Electrolyte: $\sim$200 gpl H_2SO_4, $\sim$50 gpl Zn^{++} $\sim$ 2.5 gpl Mn^{++}
No additives, C. density; 65 asf, C. temp.; 45°C, 2 hour deposit.

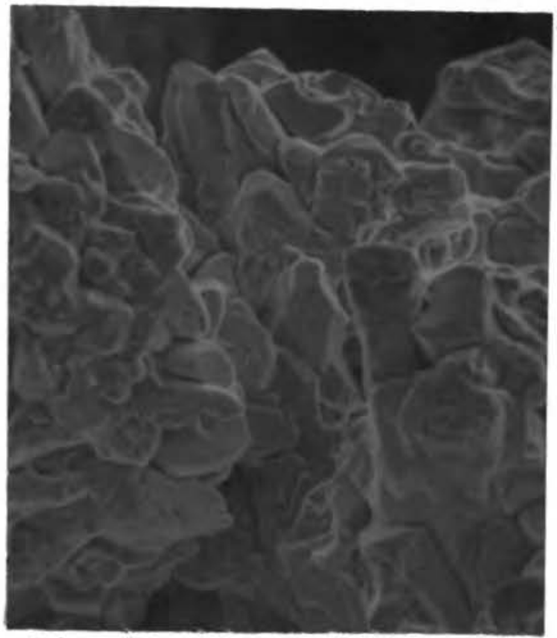

Fig. 12 - Run-No 100-3, 300X

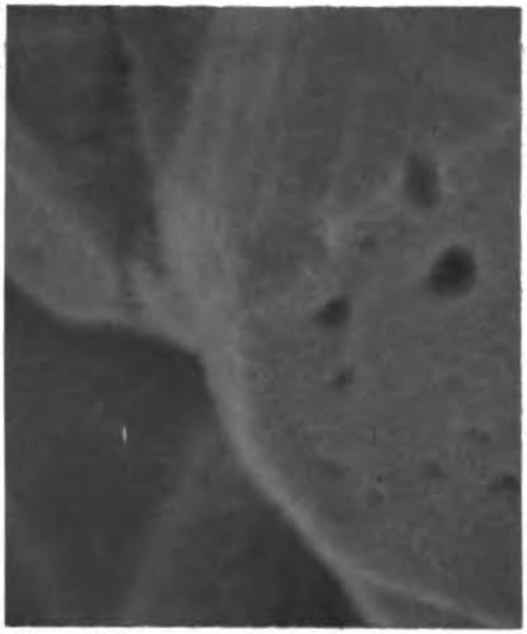

Fig. 13 - Run-No 100-3, 3,000X

Commercial Electrolyte: ~ 200 gpl H_2SO_4, ~ 50 gpl Zn^{++}; ~ 2.5 gpl Mn^{++};
No additives, C. density; 65 asf, C. temp.; 65°C, 2 hour deposit.

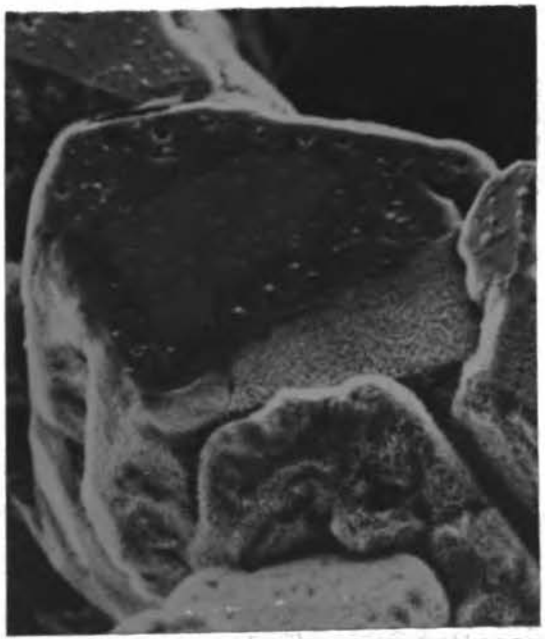

Fig. 14 - Run-No 101-1, 1,000X

Commercial Electrolyte: Animal glue; 0.01 mg/g, 2 hour deposit.

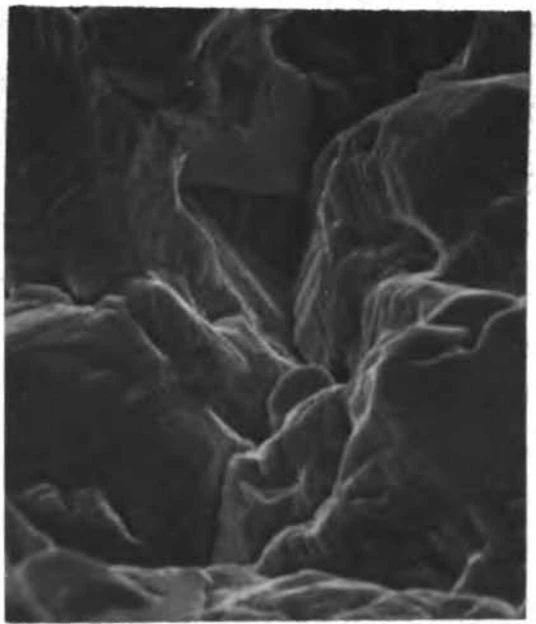

Fig. 15 - Run-No 101-2, 1,000X

Commercial Electrolyte: Animal glue; 0.10 mg/g, 2 hour deposit.

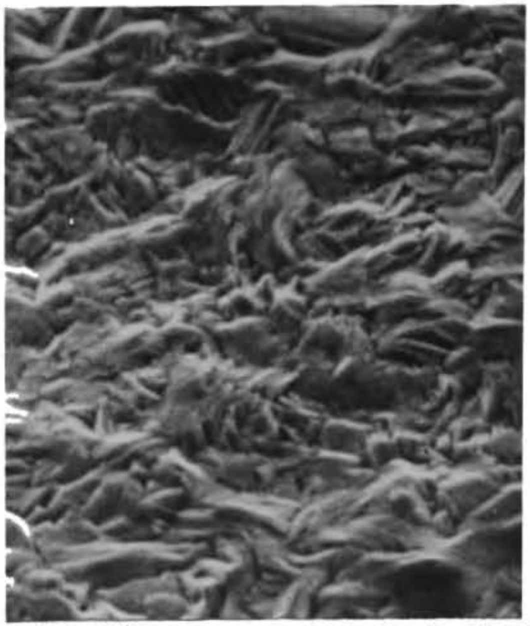

Fig. 16 - Run-No 101-3, 1,000X

Commercial Electrolyte: Animal glue; 1.0 mg/g, 2 hour deposit.

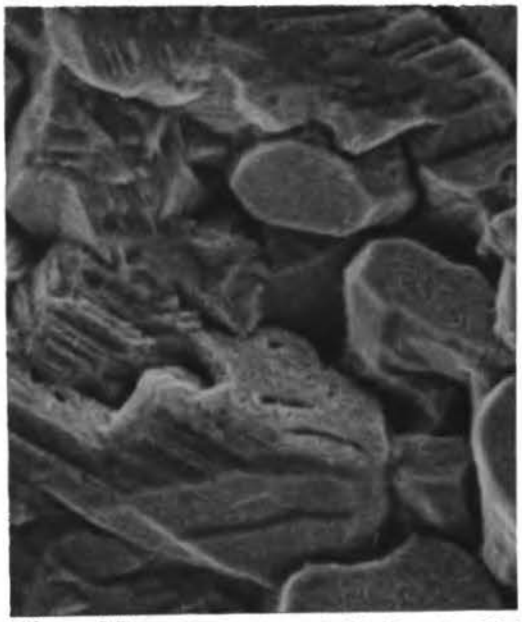

Fig. 17 - Run-No 102-1, 1,000X

Commercial Electrolyte: Sodium silicate; 0.1 mg/g, 2 hr. deposit.

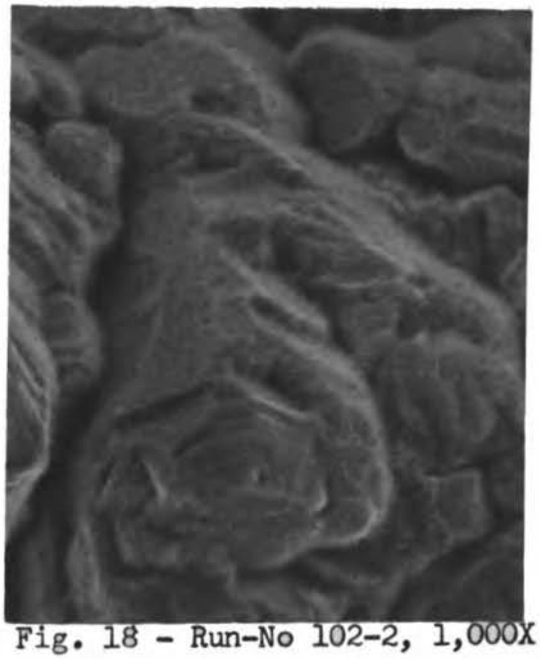

Fig. 18 - Run-No 102-2, 1,000X

Commercial Electrolyte: Sodium silicate; 1.0 mg/g, 2 hour deposit.

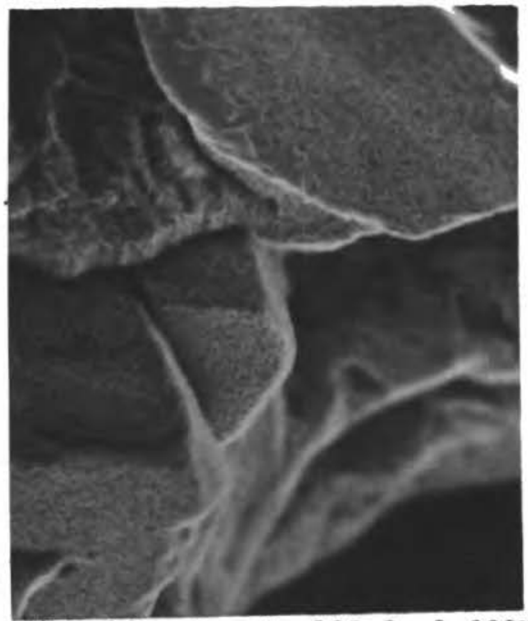

Fig. 19 - Run-No 102-3, 1,000X

Commercial Electrolyte: Sodium silicate; 10.0 mg/g, 2 hour deposit.

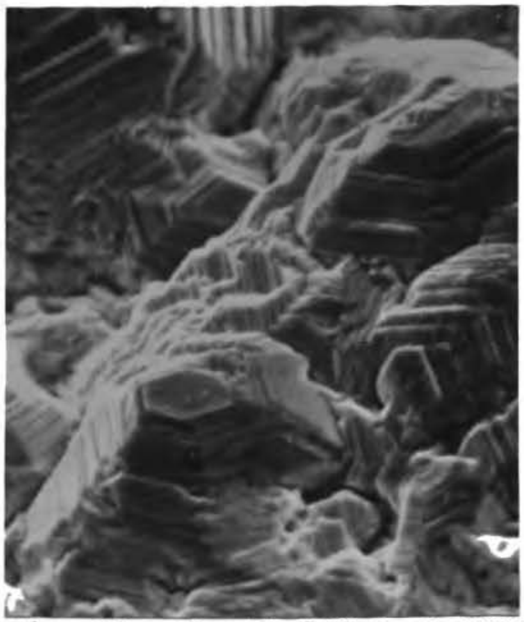

Fig. 20 - Run-No 103-3, 1,000X

Commercial Electrolyte: Gum arabic; 0.01 mg/g, 2 hour deposit.

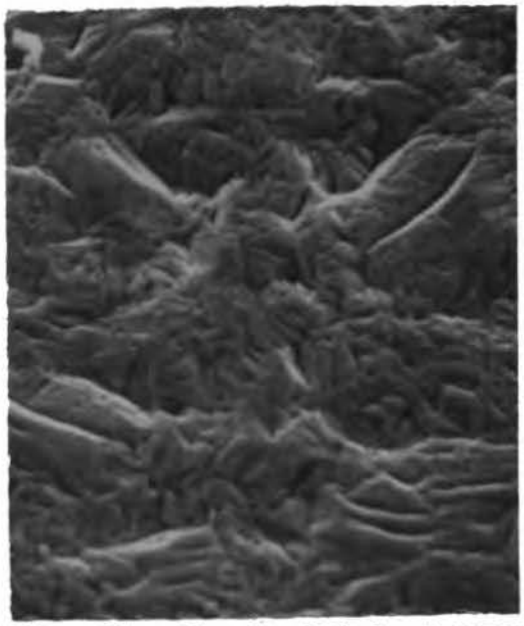

Fig. 21 - Run-No 103-1, 1,000X

Commercial Electrolyte: Gum arabic; 0.05 mg/g, 2 hour deposit.

Fig. 22 - Run-No 103-2, 1,000X

Commercial Electrolyte: Gum arabic; 0.1 mg/g, 2 hour deposit.

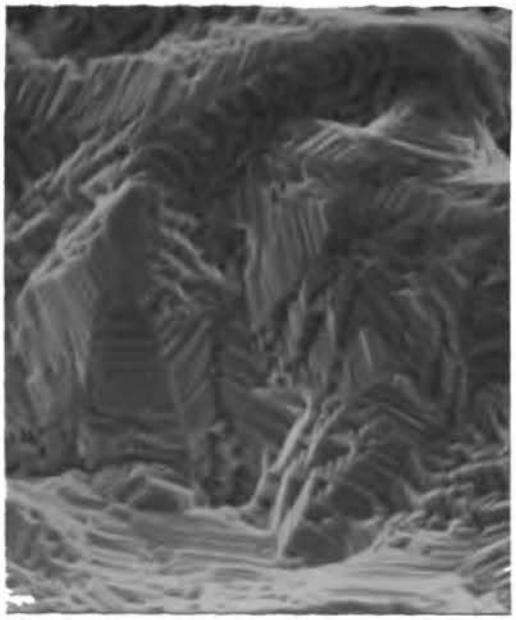

Fig. 23 - Run-No 104-2, 1.000X

Commercial Electrolyte: Animal glue; 0.2 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

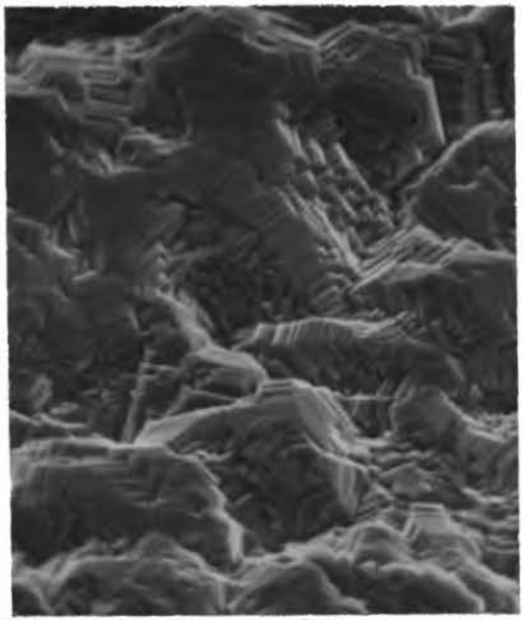

Fig. 24 - Run-No 104-3, 1,000X

Commecial Electrolyte: Animal glue; 0.4 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

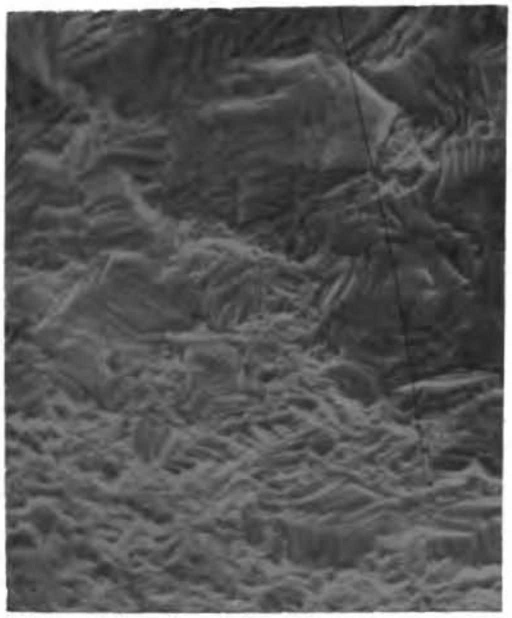

Fig. 25 - Run-No 104-4, 1,000X

Commercial Electrolyte: Animal glue; 0.6 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

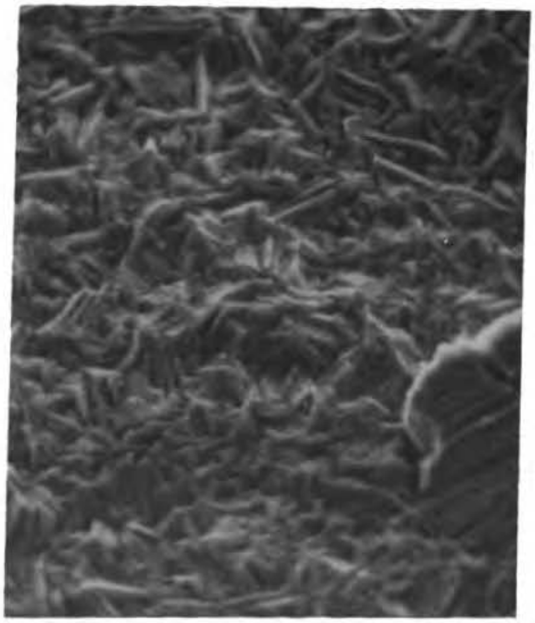

Fig. 26 - Run-No 104-5, 1,000X

Commercial Electrolyte: Animal glue; 0.8 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

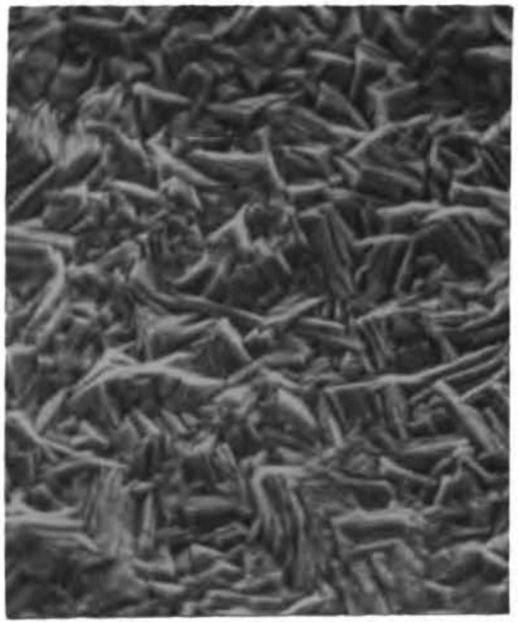

Fig. 27 - Run-No 104-6, 1,000X

Commercial Electrolyte: Animal glue; 1.0 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

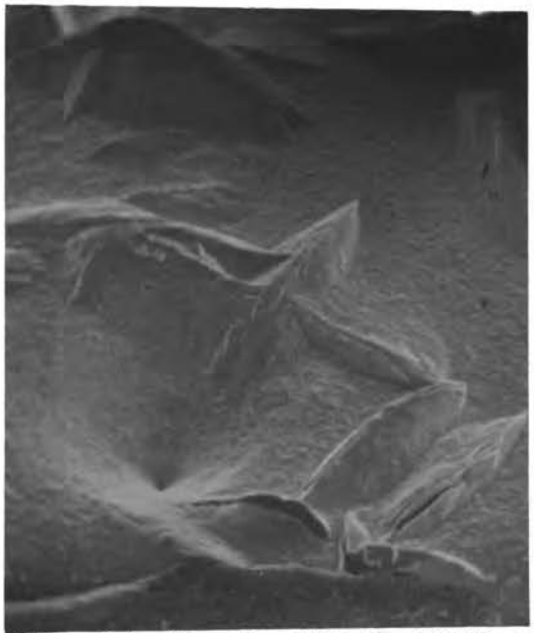

Fig. 28 -Run-No 104-5, 100X

Commercial Electrolyte: Animal glue; 0.8 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

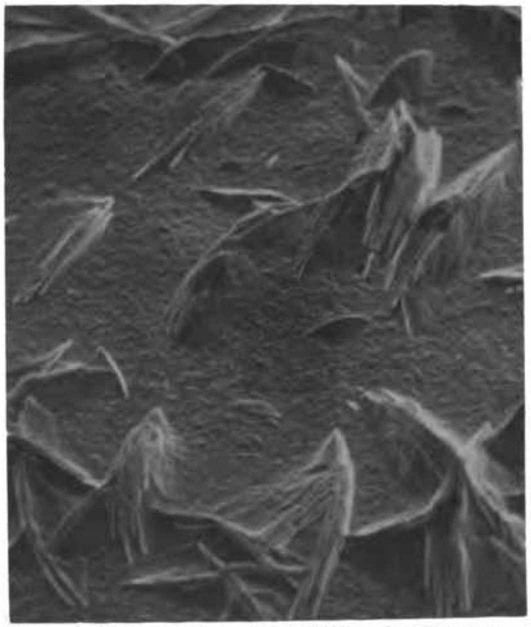

Fig. 29 - Run-No 104-6, 100X

Commercial Electrolyte: Animal glue; 1.0 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

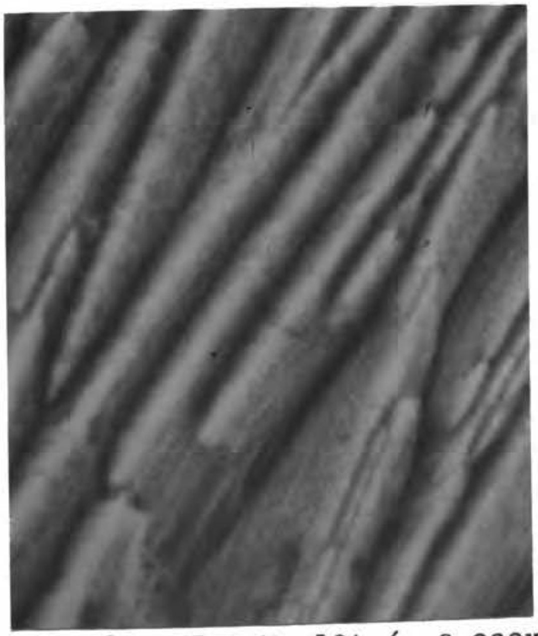

Fig. 30 - Run-No 104-6, 3,000X

Commercial Electrolyte: Animal glue; 1.0 mg/g, Sodium silicate; 0.5 mg/g, 2 hour deposit.

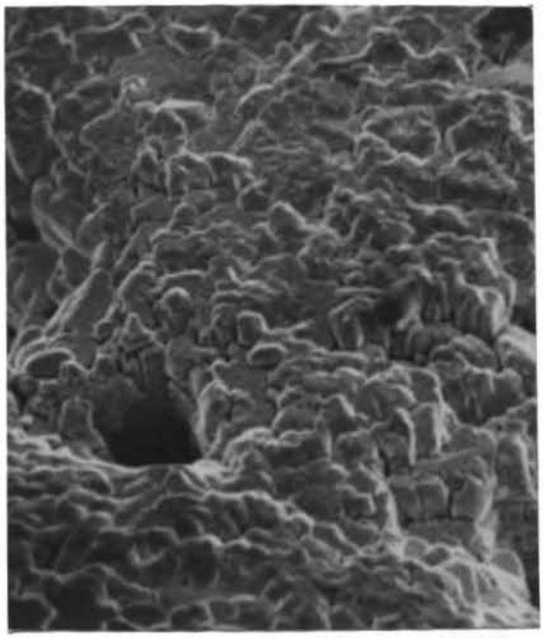

Fig. 31 - Run-No 107-3, 300X

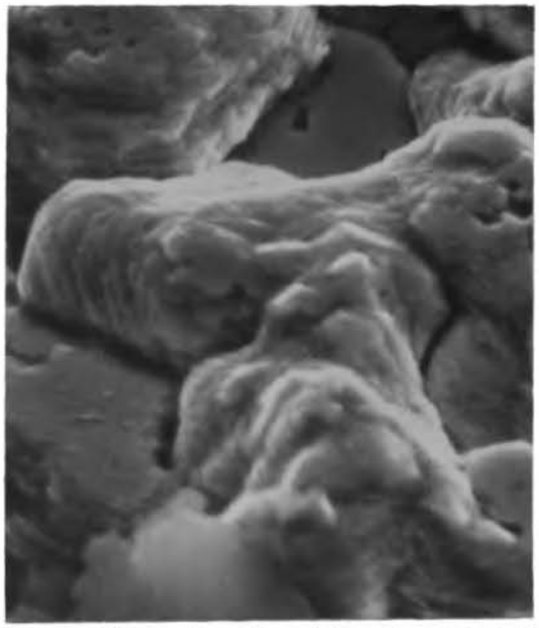

Fig. 32 - Run-No 107-3, 3,000X

Pure ZnO Electrolyte: $\sim$200 gpl H_2SO_4, $\sim$65 gpl Zn^{++}, $\sim$2.5 gpl Mn^{++},
No additives, C. density; 65 asf, C. temp.; 45°C, 2 hour deposit.

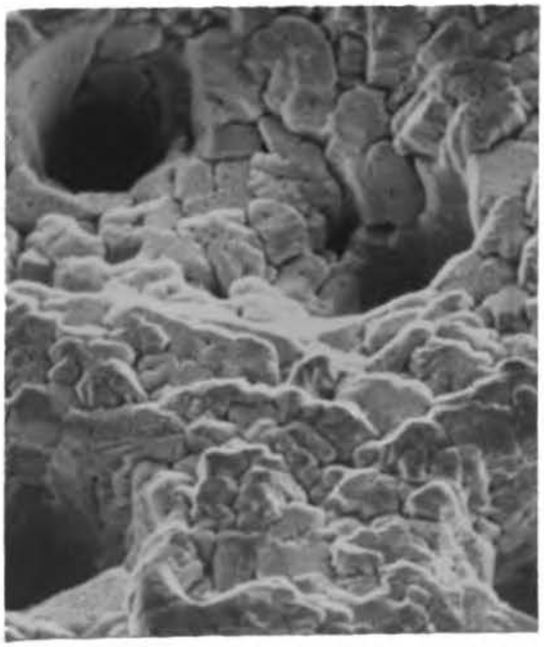

Fig. 33 - Run-No 107-4, 300X

Fig. 34 - Run-No 107-4, 3,000X

Pure ZnO Electrolyte: $\sim$200 gpl H_2SO_4, $\sim$65 gpl Zn^{++}, $\sim$3.0 gpl Mn^{++},
No additives, C. density; 65 asf, C. temp.; 45°C, 2 hour deposit.

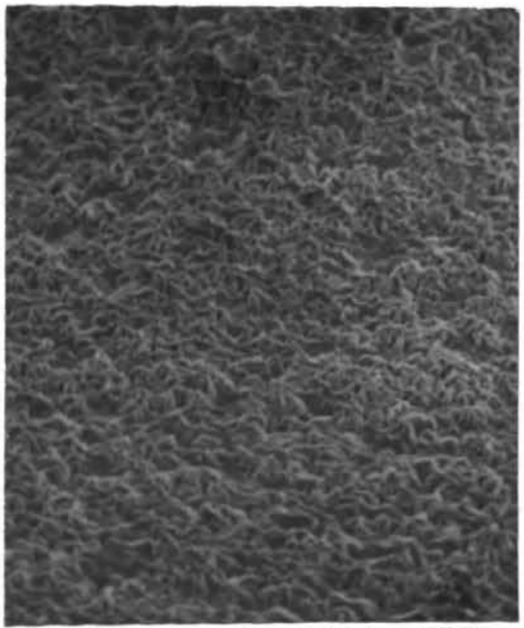

Fig. 35 - Run-No 111-1, 300X

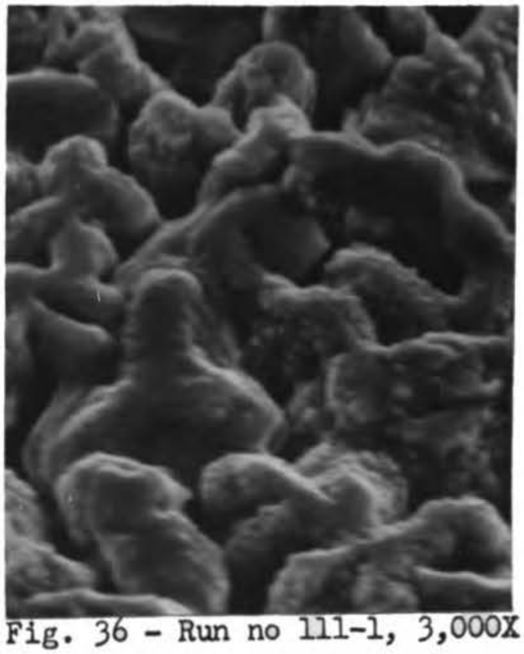

Fig. 36 - Run no 111-1, 3,000X

Pure ZnO Electrolyte: Animal glue; 0.01 mg/g, 2 hour deposit.

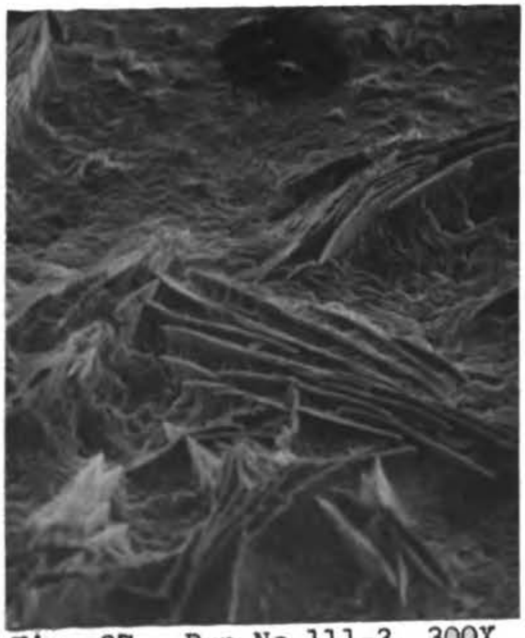

Fig. 37 - Run-No 111-3, 300X

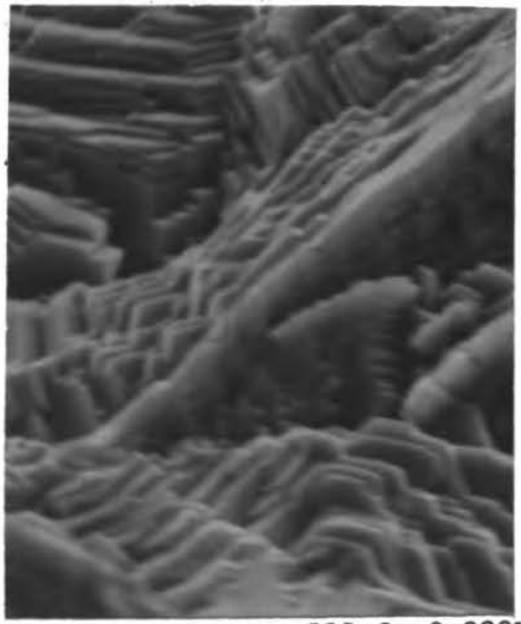

Fig. 38 - Run-No 111-3, 3,000X

Pure ZnO Electrolyte: Animal glue; 1.0 mg/g, 2 hour deposit.

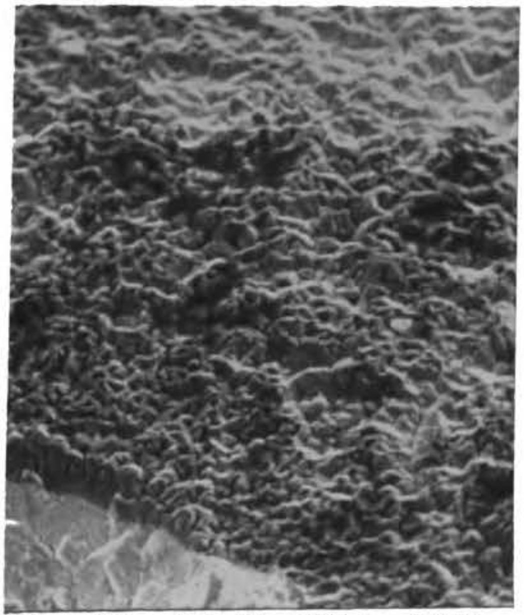

Fig. 39 - Run-No 112-1, 300X

Fig. 40 - Run-No 112-1, 3,000X

Pure ZnO Electrolyte: Gum arabic; 0.01 mg/g, 2 hour deposit.

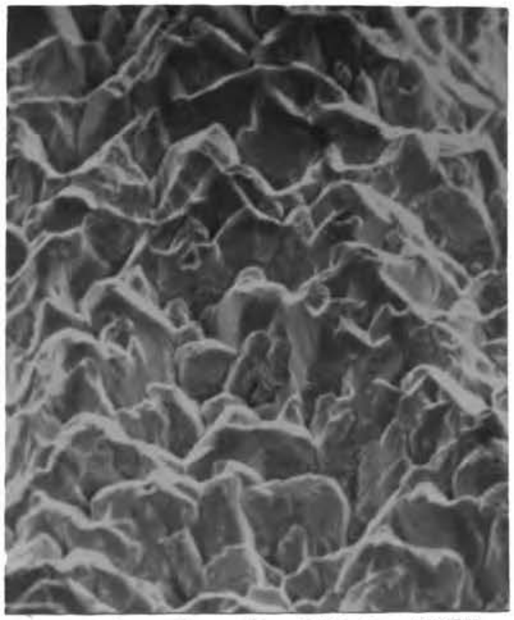

Fig. 41 - Run-No 112-3, 300X

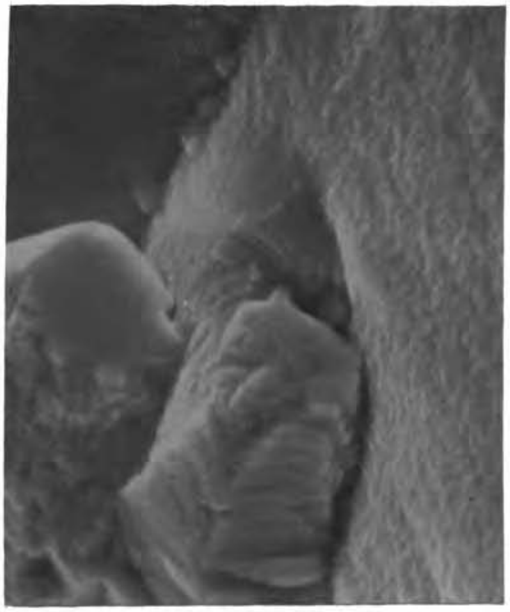

Fig. 42 - Run-No 112-3, 3,000X

Pure ZnO Electrolyte: Gum arabic; 0.10 mg/g, 2 hour deposit.

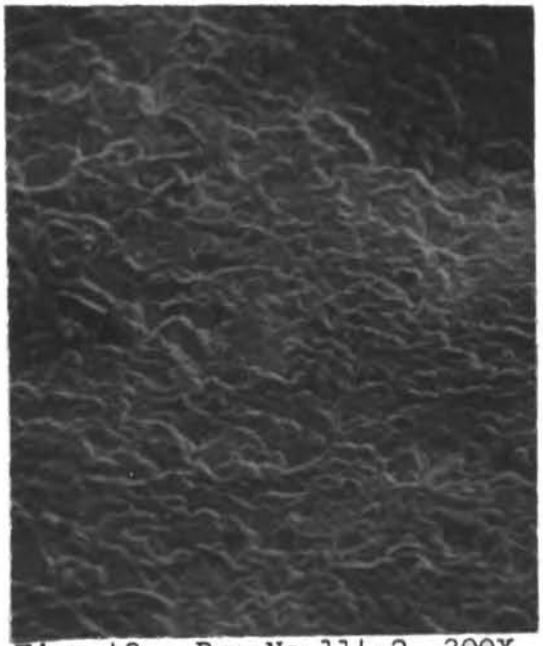

Fig. 43 - Run-No 114-2, 300X

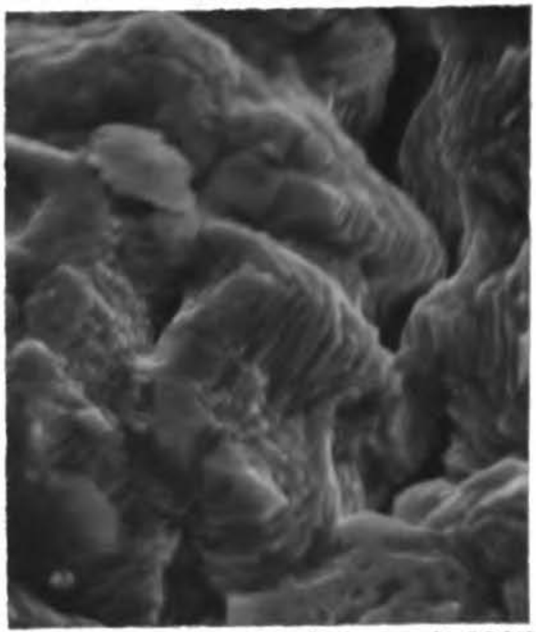

Fig. 44 - Run-No 114-2, 3,000X

Pure ZnO Electrolyte: Sodium silicate; 1.0 mg/g, 2 hour deposit.

Fig. 45 - Run-No 106-3, 300X

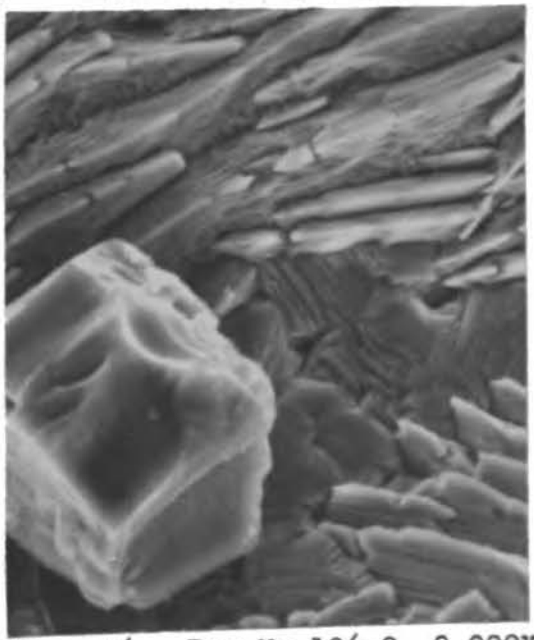

Fig. 46 - Run-No 106-3, 3,000X

Pure ZnO Electrolyte: Animal glue; 0.5 mg/g, Sodium silicate; 2.0 mg/g, 18 hour deposit.

Fig. 47 - Run-No 115-1, 1,000X

Pure ZnO Electrolyte: $\sim$250 gpl H_2SO_4, $\sim$40 gpl Zn^{++}; $\sim$2.5 gpl Mn^{++}; C. density; 95 asf, C. temp.; 60°C, No additives, 2 hr. deposit.

Fig. 48 - Run-No 115-4, 3,000X

Pure ZnO Electrolyte: $\sim$200 gpl H_2SO_4, $\sim$65 gpl Zn^{++}; $\sim$2.5 gpl Mn^{++}; C. density; 5 asf, C. temp.; 25°C, No additives, 6 hour deposit.

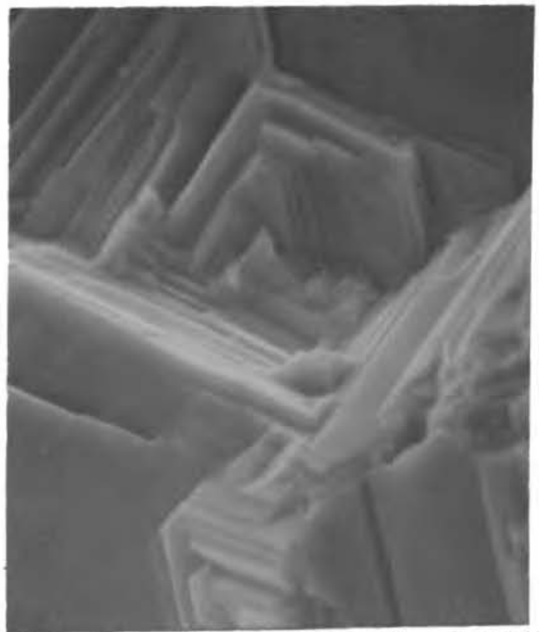

Fig. 49 - Plant Deposit, 3,000X

2 hour deposit.

Fig. 50 - Plant Deposit, 3,000X

6 hour deposit.

Fig. 51 - Plant Deposit, 3,000X

8 hour deposit.

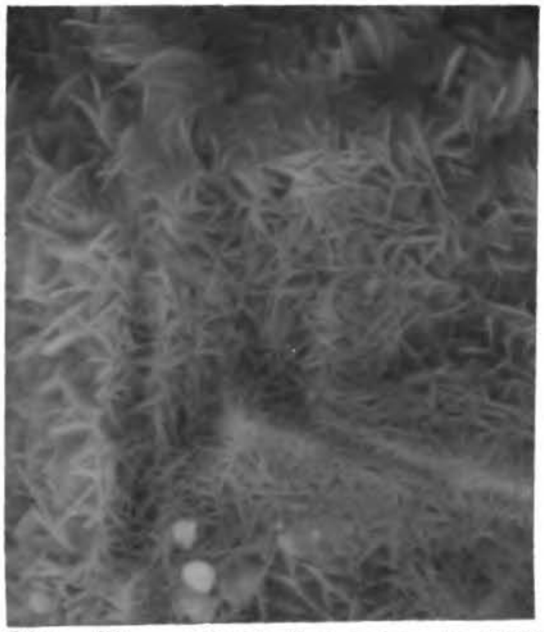

Fig. 52 - Plant Deposit, 3,000X

12 hour deposit.

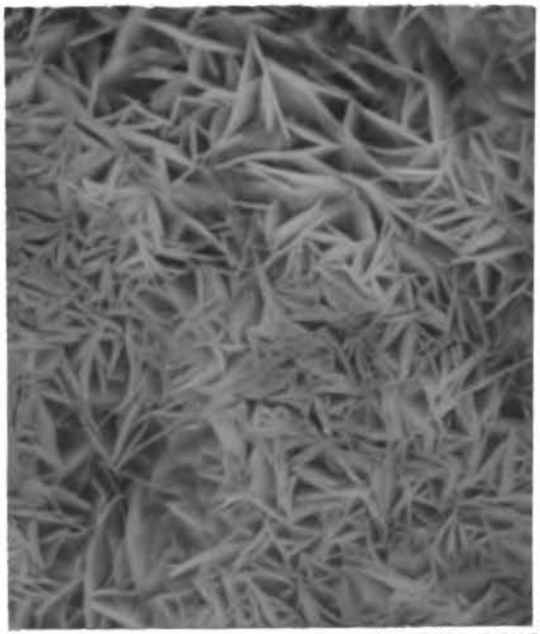

Fig. 53 - Plant Deposit, 3,000X

24 hour deposit.