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ELECTRODEPOSITION RESEARCH PROGRESS REPORT

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Date: June 1-30, 1948

Prepared by: Edward Orban

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ELECTRODEPOSITION RESEARCH GROUP

W. Abel, R. Bell, C. Neibel, E. Orban, and W. Raiff

ABSTRACT

This report contains a review of the work conducted by the Electrodeposition Group for the last six months.

Pictures and a discussion of the method used to convert production solutions of postum to hydrofluoric acid solutions of postum are given.

Attempts to plate postum in an inert atmosphere by remote control have been made. As yet no successful runs have been completed.

Standardization of normal calomel electrodes by comparison to silver-silver chloride electrodes and to hydrogen electrodes is described.

DETAILED REPORT

In view of the newly established policy of a semiannual review of each problem, this Progress Report will contain, in addition to the detailed report of progress for the month of June, the aforementioned review.

I. Plating of Postum from Hydrofluoric Acid Solutions

In the early part of this year a review of the overall problem was made, and in appraisal of the results being obtained, it was decided that the process be tried on a production size scale. The reasons for this decision were:

1. A smoother plate was formed.
2. A more adherent plate was laid down.
3. Approximately twenty times the amount plated out of nitric acid could be plated out of hydrofluoric acid.

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4. The neutron counts of these foils were as good as if not better than, counts of foils out of nitric acid solutions.

5. Equivalent quantities of postum could be plated out of hydrofluoric acid in much less time than out of any other solvent.

Since that time equipment has been constructed and trial runs have been carried out.

A. Plate Quality

1. Neutron Emission

Review

Comparative data shows that foils plated out of hydrofluoric acid solutions have neutron counts slightly lower than those prepared from nitric acid solutions. Consistent neutron counts of from 0 to 70 neutrons /unit/second can be obtained for low density foils (less than 8 units per cm.²) plated out of hydrofluoric acid. Table I shows comparative sets of foils plated from the two solutions.

Neutron counts on the same foil over a period of six months show a wide variation. Table II illustrates the randomness of the counts.

This foil has been sealed in an inert atmosphere; hence, the only possible variable would seem to be in the counting technique.

The effect of oxygen on the neutron counts is being studied with the use of an "inert" plating unit. The entire plating operation is carried out by remote control in an inert atmosphere. (See "Inert" Plating Unit in this Progress Report).

2. Adherence of Plate

Review

A "shaker" test has been devised to test the adherence of postum plate. The foils are placed in a container and shaken vigorously for a five hour period. Calorimetric values of the foils before and after the "shake" test have been determined. To date results have shown that foils plated from hydrofluoric acid solutions lose less than five per cent during the test. Comparative tests will be run on foils plated from nitric acid solutions.

3. Photographic Examination of Foils

This problem has been deferred temporarily for more urgent work.

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Table I

NEUTRON COUNTS OF POSTUM FOILS

<u>Plating Medium</u>	<u>Foil Number</u>	<u>Neutron Counts/Unit/Sec.</u>
1.5 N nitric acid	533	112
1.5 N nitric acid	534	61
1.5 N nitric acid	536	63
1.5 N nitric acid	537	65
1.5 N nitric acid	538	0
1.0 N hydrofluoric acid	539	96
1.0 N hydrofluoric acid	540	96
1.0 N hydrofluoric acid	541	23
1.0 N hydrofluoric acid	542	43
1.0 N hydrofluoric acid	543	27
1.0 N hydrofluoric acid	544	26

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Table II

STUDY OF NEUTRON COUNTS WITH TIME

<u>Foil Number</u>	<u>Date</u>	<u>Neutrons/Unit/Second</u>
395	1/30/48	84
395	2/12/48	60
395	2/20/48	112
395	3/15/48	40
395	5/11/48	153
395	6/16/48	95

4. "Inert" Plating Unit - W. Raiff

Progress for June 1948

The "inert" plating unit, details of which are given in the Progress Report of the Electrodeposition Research Group, November 16-30, 1947, has been put into operation. The plating control lines were wired to the panel board, and a helium and a nitrogen system were installed. Two preliminary runs were carried out.

Run No. 1 was plated directly from a production solution obtained from Unit IV which contained approximately 1.26 units per 10 ml. The current density was rather high (about 4 ma./cm.²), and the resulting plate was black. A fault in the canning process caused a failure before any measurements could be made.

Run No. 2 was a duplication of the first run. A one second exposure to the atmosphere was the only error in an otherwise successful run. Complete data are lacking, but a total of 576 neutrons/seconds was measured on the foil. This rather high result may be due to a

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contaminant such as stopcock grease or oxygen.

Future Plans

Runs in which air, stopcock grease and other contaminants are eliminated will be made.

B. Solution Conversion - R. Bell

1. Conversion of Production Solutions to Bismuth-free Postum Solutions of Hydrofluoric Acid

Review

The plating of postum out of hydrofluoric acid creates the problem of handling "hot" hydrofluoric acid solutions, and the conversion, in suitable apparatus, of nitric acid solutions to hydrofluoric acid solutions.

The following method has been conceived for the conversion of a nitric acid solution to a hydrofluoric acid solution. A production solution of postum (approximately 1.5 N nitric acid) is treated with excess sodium carbonate, resulting in the precipitation of postum carbonate and bismuth carbonate. These two solids are separated from the liquid and are digested with hydrofluoric acid. A large share of the bismuth fluoride, formed by the reaction of the carbonate with hydrofluoric acid, remains insoluble, while a large share of the postum fluoride formed the same way goes into solution.

The apparatus to handle the solutions was constructed entirely out of "Polystyrene" and "Teflon" plastics. It was found that "Teflon" itself was an efficient filter medium which did a better job than either sintered silver or sintered stainless steel.

Runs have been made with solutions containing only bismuth and with production solutions containing both bismuth and postum. The "cold" runs with bismuth were made in order to determine the efficiency of removal of bismuth by the process. It was found that only about eighteen per cent of the original amount of bismuth appeared in the final solution.

An average of the "hot" runs using about five units per run gave only a 71.5 per cent yield. The remainder was found in other parts of the equipment. With a solution containing seventeen units

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a 66.5 per cent yield was obtained.

From the above considerations, it is evident that the course of investigation should be directed toward improving the yield.

Progress for June, 1948

The apparatus used for the preparation of hydrofluoric acid solutions from the production nitric acid solutions is shown in Figure 1. It is operated as follows:

- a. A production solution containing 20-25 units in 100 ml. of 1.5 N nitric acid is placed in the SAMPLE RECEIVER.
- b. The sample is transferred to the REACTION BOTTLE.
- c. Saturated sodium carbonate solution is added from the Na_2CO_3 RESERVOIR until effervescence ceases and a precipitate forms, after which a slight excess of sodium carbonate is added. The solution in the reaction bottle is stirred during this neutralization using a platinum covered magnetic stirrer.
- d. The stirring is stopped and the precipitate is allowed to settle to the bottom of the REACTION BOTTLE.
- e. The supernatant liquid is drawn off through the TEFLON FILTER (shown in Figure 2) into the VACUUM BOTTLE. The precipitate is washed twice with about 75 ml. of water run in from the WATER RESERVOIR. These washings are drawn over into the VACUUM BOTTLE in the same manner.
- f. The collected first filtrate and washings are drawn out of the VACUUM BOTTLE through the PRODUCT TAKEOFF. The vacuum bottle is rinsed by evacuating and allowing water from the WATER RESERVOIR to enter the RINSE LINES. (This solution is designated as the First Filtrate.)
- g. The precipitate remaining in the REACTION BOTTLE, consisting of postum carbonate and bismuth carbonate, is leached with 10 ml. of 10 N hydrofluoric acid from HF PREHEATER which heats the hydrofluoric acid to 60°C. before it enters the REACTION BOTTLE. The leaching requires one-half hour with stirring while the solution is maintained at 60°C. by the PLATINUM HEATER. (See Figure 2).

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APPARATUS FOR PREPARATION OF BISMUTH FREE POSTUM IN HYDROFLUORIC ACID SOLUTION

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h. The solution is allowed to cool for one-half hour with continued stirring, after which the precipitate is allowed to settle.

i. The supernatant liquid is drawn off into the vacuum bottle, and the precipitate is washed twice with 20 ml. of water each time. The filtrate, washings and vacuum bottle rinse are collected as before. (Second Filtrate). Theoretically, all the activity should be concentrated in this solution.

j. The remaining precipitate in the reaction bottle is dissolved in 20 ml. concentrated nitric acid and pulled through the system in the same manner as the other two solutions. (This is designated as the Precipitate Solution.)

Three analyses of cold bismuth runs have been made. One has been previously reported (Electrodeposition Research Group Progress Report for May 1-31, 1948), but for the sake of comparison it will be repeated here. The method of analysis is the same as reported for the first run. Table III shows the results of the runs.

Table III

BISMUTH IN THE CONVERSION OF 1.5 N NITRIC ACID TO 1.0 N HYDROFLUORIC ACID

	Run #1	Run #2	Run #3
Original Solution	0.1016 gm.	0.1016 gm.	0.1016 gm.
Bismuth in First Filtrate	0.0172 gm.	0.0318 gm.	0.0111 gm.
Bismuth in Second Filtrate	0.0102 gm.	0.0216 gm.	0.0235 gm.
Bismuth in Precipitate Solution	0.0610 gm.	0.0420 gm.	0.0564 gm.
Per Cent of Bismuth Remaining in Hydrofluoric Acid Solution	16.9	31.0	10.9

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The bismuth unaccounted for went out of the analyses through its slight solubility in hydrofluoric acid, and through the small amount that passed through the "Teflon" filter.

The solubility of bismuth fluoride in hydrofluoric acid was determined by dissolving 5.0084 gm. of bismuth oxide in 20 ml. of 15 N nitric acid. One ml. aliquots were placed in a centrifuge tube, neutralized by the addition of saturated sodium carbonate, and then centrifuged for ten minutes. The supernatant liquid was decanted, the residue washed and centrifuged again. After the second washwater was decanted, 5 ml. of 10 N hydrofluoric acid was added to the residue. After a vigorous shaking, the suspended material was centrifuged out, and 5 ml. was decanted into a platinum dish. The solution was evaporated to dryness and weighed. There was 0.0007 gm. of bismuth fluoride soluble per ml. of 10 N hydrofluoric acid.

Approximately 0.0070 gm. of bismuth fluoride would be dissolved in the 10 ml. of 10 N hydrofluoric acid used to leach the precipitate during the analyses. Since the loss was much greater than this, the majority of the loss must be attributed to the pore size of the "Teflon" filter or to the extremely small particle size of the bismuth fluoride.

A production solution containing 17.3 units was run through the apparatus according to the procedure described earlier in this report. A yield of 66.5 per cent resulted.

Table IV

PROCESSING OF A POSTUM SOLUTION IN THE CONVERSION UNIT

	Units of Postum
Starting Material	17.3
Postum in First Filtrate	0.0141
Postum in Second Filtrate	11.5
Postum in Precipitate Solution	0.75
Postum Unaccounted for	5.1

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Future Plans

Effort will be concentrated on trying to improve the postum yield to a value comparable to processes in use in production. It is hoped that at the same time the amount of bismuth in the plating solution may be further reduced.

2. Conversion of Hydrofluoric Acid Residues and Rinses to Nitric Acid Solutions for Return to Unit IV

Review

In order to reprocess solutions in the production lines at Unit IV, the residual solutions returned to them must be free of hydrofluoric acid because of glass lined equipment used in the process. Necessarily, all hydrofluoric acid solutions used by the Electrodeposition Research Group must be converted into solutions free of this material.

A process, similar to that used in the past by the Process Research Group, (Seminar Paper for April 1, 1946 by Carl Rollinson) has given results showing better than 99.9 per cent recovery.

These results are satisfactory for all practical purposes, and the practice has been reduced to routine. Therefore, the research on this problem is considered to have reached a satisfactory conclusion.

II. Plating of Postum from Nitric Acid and Other Media

During the plating of postum out of hydrofluoric acid solutions, several runs have been made plating postum out of nitric acid for comparison purposes only. The following points were observed:

1. Under the same conditions the percentage of material plated out of nitric acid was about the same as the percentage plated out of hydrofluoric acid.
2. A higher line voltage and a higher amperage was observed using nitric acid solutions.
3. The appearance of postum plated out of hydrofluoric acid was light gray with a sheen on the surface; whereas, that plated from nitric acid was dark gray to black.

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4. The neutron counts of the metal plated from hydrofluoric acid was slightly better than those from nitric acid.

5. It was possible to plate ten to twenty times as much postum out of hydrofluoric acid as out of nitric acid.

III. Solubility of Postum in Various Media

Review

The solubility of postum in various concentrations of nitric acid was determined at 25.4°C. ambient temperature. The heating effect of postum was taken into account in plotting the curves. It was found that the solubility in 1.0 N and 1.5 N nitric acid dropped very sharply with time. Previously, it had been postulated that the high flux of alpha particles was destroying the acid, but a determination of the acid strength of each of the two solutions that had been under alpha bombardment for one month showed that it remained unchanged. Another possibility is that a change of solid phase occurs, and that the true solubility cannot be reached until the particles are large enough to precipitate.

IV. Miscellaneous

A. Preparation and Testing of Standard Cells

Review

The purity of the deposit of postum is important in that it effects the other properties of the plate such as adherence, neutron emission, etc. In order to control the purity, it is necessary to plate the material at a potential which will exclude the electrodeposition of as many materials as possible, particularly bismuth. It has been determined that the best potential at which to maintain the cathode is zero with respect to the normal calomel electrode. (See Information Report No. 22 by Dr. M. M. Haring). It is essential, therefore, that a reliable method of checking the potential of the reference electrode be developed. Since most of the work occurred during this past month, it will be reported in detail under the section below titled Progress for June, 1948.

Progress for June, 1948

Twelve calomel electrodes were prepared for use in plating processes. To check these cells, six hydrogen electrodes were made

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and checked against the calomel half cells. The cell is

Obviously this cell cannot be used for calibration of the calomel half cell because of the liquid junction for which no correction is made. Table V shows the results of the intercomparison of all the calomel half cells with the No. 1 hydrogen half cell.

Table V

HYDROGEN - CALOMEL CELL

<u>Calomel Cell No.</u>	<u>Measured Potential</u>	<u>Theoretical Potential</u>	<u>Difference</u>
1	0.2864	0.2838	0.0026
2	0.2887	"	0.0049
3	0.2882	"	0.0044
4	0.2877	"	0.0039
5	0.2865	"	0.0027
6	0.2839	"	0.0001
7	0.2844	"	0.0006
8	0.2869	"	0.0031
9	0.2882	"	0.0044
10	0.2880	"	0.0042
11	0.2895	"	0.0057
12	0.2883	"	0.0045
		Average	0.0034

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These results are not in good agreement and indicate that the cells are probably not at equilibrium. The average deviation may be a measure of the liquid junction potential but no conclusions can be drawn from the results.

In order to avoid the liquid junction in the above cell, the following cell was devised:

So that the correct potentials of the silver half cell could be determined, they were compared against a hydrogen half cell,

Table VI shows the results of the three silver half cells compared to the hydrogen half cell number 5.

Table VI

STANDARDIZATION OF SILVER-SILVER CHLORIDE HALF CELL

<u>Electrode No.</u>	<u>Measured Potential</u>	<u>Theoretical Potential</u>	<u>Difference</u>
0	0.2295 N	0.2295	0
1	0.2293	0.2295	-0.0002
4	0.2293	0.2295	-0.0002

These cells show excellent agreement among themselves and with the theoretically calculated value, and can be presumed to be correct.

The comparison of the silver half cells against the normal calomel half cells is shown in Table VII.

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Table VII

STANDARDIZATION OF CALOMEL HALF CELLS

Calomel Half Cell Number	Silver-Silver Chloride Half Cell			ΔE
	#0	#1	#4	
1	0.405	0.0412		0.0047
2	0.414	0.422	0.424	0.0040
3	0.397	0.394		0.0030
4	0.419	0.419		0.0058
5	0.405	0.405		0.0033
6	0.0367	0.0369		0.0047
7	0.0338	0.0343	0.0347	0.0083
8	0.0411	0.0420	0.0420	0.0109
9	0.0403	0.0415	0.0413	0.0032
10	0.0375	0.0384	0.0384	0.0037
11				0.0068
12	0.0356	0.0364	0.0364	0.0088

The last column shows the difference between the theoretical potential, calculated to be 0.0452 volts, and the potential measured between the normal calomel half cells and the No. 1 Silver-Silver Chloride Half Cell.

Further work will be required to produce cells than can check better than 10 millivolts, preferable to within 1 millivolt.

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