THE EFFECT OF ADDITION AGENTS ON SURFACE SMOOTHNESS OF ELECTROLYTIC NICKEL

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THE EFFECT OF ADDITION AGENTS ON SURFACE SMOOTHNESS OF ELECTROLYTIC NICKEL

By

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GENERAL INTRODUCTION

Addition agents, in the broadest sense, include all substances other than the metallic salt and water which are added to a bath for any purpose whatever. Generally speaking, however, the term is used to define only those substances which have an influence on the structure of the deposit, and thus substances added for the purpose of controlling conductivity and metal and hydrogen ion concentration are excluded. Addition agents have been classified in several ways by various investigators. Blum[2] divides these compounds into two classes, viz., colloidal and crystalloidal, but as he says, this distinction is inadequate since many crystalloidal substances cause the formation of colloids in solution. More recently in an article by W. L. Penner, G. Soderberg and E. M. Baker[12], addition agents are divided into two fairly distinct classes. Class I is represented by cobalt salts, and by aryl sulfonic acids, preferably polysulfonic acids, and aryl sulfonamides and aryl sulfonimides. The concentration of this class of compounds is only limited by their solubility, for after an optimum concentration, further additions cause no change in the appearance or properties of the deposit. The second class is represented by cadmium and zinc, sodium formate, aldehydes and ketones, and amino poly aryl methanes. A critical concentration is usually present for members of this class as an excess has detrimental effects on such properties as appearance, adhesion, and throwing power. This division of addition agents was the most

logical classification encountered by the author and consequently will be utilized throughout this investigation.

Several theories explaining the beneficial action of addition agents have been proposed, but regardless of the process, the ultimate effect is the formation of finer-grained deposits, resulting in smoother, more lustrous surfaces. Organic addition agents have been used extensively in nickel plating only in the last few years as they are difficult to control and were thus considered impractical by earlier investigators. The modern addition agents are still somewhat troublesome to control, but their effect in producing a much smoother ductile deposit more than compensates for this disadvantage.

In this project, representative addition agents of Class I and Class II were used, as indicated later under each specific phase of the investigation, in two common commercial nickel baths, viz., Watts Type and High Chloride, the constituents of which are shown in Table I. In addition, two salt constituents of the above baths were used separately as standard solutions in Part III of this investigation and are designated as Chloride and Sulfate in Table I.

TABLE I

COMPOSITION OF STANDARD BATHS

	Watts Type Bath g./l	High Chloride Bath g./l	Chloride Bath g./l	Sulfate Bath g./l
Nickel sulfate, $NiSo_4 \cdot 6 H_2O$	300	75	---	367
Nickel chloride, $NiCl_2 \cdot 6 H_2O$	60	225	332	---
Total nickel, Ni	82	72	82	82
Boric acid, H_3Bo_3	40	40	---	---

It was naturally impossible to study all the effects of these addition agents and thus it was decided to investigate primarily their effect on surface smoothness. In addition, however, the author also investigated their effect on Current Density--Potential Curves, and Cathode Efficiencies, the results of which are not only important in themselves but also can be used in conjunction with future research dealing with throwing power and similar problems. The present investigation is thus divided into three more or less distinct parts: I. Surface Smoothness, II. Current Density-Current Efficiency Relationships and, III. Current Density-Potential Measurements.

INTRODUCTION

PART I: The Effects of Addition Agents on Surface Smoothness

According to W. L. Penner, G. Soderberg, and E. M. Baker[12], some of the organic compounds of Class I addition agents, produce bright plates by themselves, while others may decrease grain size but produce no apparent brightness or smoothing effect. However, all of these compounds have the ability to carry a larger amount of addition agents of Class II and enhance their action. Class II compounds are seldom used by themselves in modern nickel plating as they produce either too brittle a plate or a plate of insufficient smoothness and brightness. It is thought that the most brillant plate and those which exhibit the greatest degree of smoothing out of the plate over imperfections in the subsurface are obtained, when a material of the first class is used in conjunction with a material of the second class which is so active as to cause brittleness and poor adhesion when used alone. One cannot proceed too far in this direction, however, with Class II compounds, because the carrying ability of Class I is limited not only to Class II compounds but also organic and inorganic impurities that adversely effect the plate.

Many investigators have studied the effects of various addition agents used in modern bright nickel baths. Zinc, a member of Class II, has been an important constituent in nickel baths for many years.

It is not accurately known when zinc was first added to nickel solutions but C. H. Proctor[13], mentioned its use in 1915, and it has been used rather extensively ever since as an addition agent for the production of smoother bright deposits. Many organic addition agents have also been investigated in the last few years. L. L. Linick[8], found that benzoyl acetic, diphenyl acetic, phenyl acetic, benzenesulfonic, toluic and tropic acids produced no satisfactory smoothness or brightness of deposit. E. Raub and M. Wittum[14], investigated certain aromatic nitrogen compounds and found that aromatic amines had no appreciable effect. Saccahrin in concentrations of 0.1 - 0.2 g./l. and methylene blue produced brilliant deposits.

The same authors also made an intensive investigation of aromatic and heterocyclic sulfonic acids. Alpha and beta naphthalene sulfonic acids were very effective in smoothing over the surface irregularities and forming a bright deposit. In the heterocyclic field, furfural, pyridine and orthohydrozyquinoline were investigated and results indicated that the first and last were the best brighteners. Stout[16], and Springer[15], found that aromatic sulfonic derivatives were important addition agents. Young[22], mentioned the use of naphthalene trisulfonic acid, sulfonated oleo resins, and benzene or o-toluene sulfonamides as effective brighteners. Many other investigators such as Watts[20], Ballay[1], Hendricks[6], and Meyer[9], have investigated addition agents in nickel baths, but as voluminous as is the literature, little has been mentioned concerning the specific "hiding" or "smoothing power" of modern bright nickel addition agents.

In this phase of the investigation, therefore, the primary goal was to determine the power of certain Class I and Class II addition agents used in bright nickel plating to smooth over surface roughness of buffed steel and in consequence produce a brighter deposit. It is logical, of course, that the brighter a deposit the smoother it is, but it is impossible to judge relative brightness or smoothness visually. Thus, in accomplishing the purpose of this phase, use was made of a comparatively new instrument in the plating field, viz., "The Brush Surface Analyzer" which rapidly measures the width, spacing, and depth of surface irregularities from a fraction of 1 microinch (.000001) to 3000 microinches. This instrument makes it possible to analyze surfaces accurately and rapidly and thus provides an effective means of comparing the smoothing effect of addition agents in bright nickel plating. The addition agents selected for this work were sodium o-benzoyl sulfimide and benzene sulfonamide of Class I, and zinc, in the form of zinc sulfate ($ZnSO_4 \cdot 7H_2O$), and allyl-chloracetate quaternary of pyridine (PQ) as representatives of Class II addition agents.

DESCRIPTION OF INSTRUMENT

A photograph of the model SA-2 Brush Surface Analyzer is shown on page 8a. The instrument consists of three main parts: the motor driven Pick-Up Arm, the Calibrating Amplifier, and the Direct Inking Oscillograph. The Pick-Up Arm contains a piezo-electric crystal element which is connected through a lever system to a diamond stylus which rises over and falls into surface irregularities as it moves back and forth over the specimen under test. As the Pick-Up Arm moves back and forth in a ten second cycle, the vertical motion of the stylus bends the crystal. When this occurs, the crystal generates a voltage, the polarity of which depends upon the direction of the stylus movement. These stylus movements are then amplified and reproduced from 1 to 500 cycles per second by the Calibrating Amplifier. This amplification then actuates the pen motor located in the Direct Inking Oscillograph which in turn drives the inking pen over a moving paper chart. The chart is drawn beneath the recording pen by a constant speed motor and a selective gear train, giving a choice of three speeds. These are 5 mm., 25 mm., and 125 mm. per second equivalent to approximately 0.2 inch, 1 inch, and 5 inches respectively. The slowest speed was used throughout this investigation. The resulting Profilographs as shown in Figures 1-38 are profile pictures of the surfaces under test. Each graph shows four main parts: (1) calibration of surface before plating (2) profile of surface before plating (3) calibration of surface

after plating (4) profile of surface after plating. The calibration is important in that it indicates whether or not the Pick-Up Arm is parallel to the surface to be explored. The Pick-Up Arm is considered correct if a pen oscillation (peak to peak deflection) is between 10 - 20 chart divisions when the Arm is raised 1/8 inch and then allowed to fall back on the surface. In addition, the B. L. 105 R.M.S. Meter Attachment is a useful accessory to this instrument as it rapidly assigns a numerical value to a surface under investigation. This meter is the "average reading" type, calibrated in terms of the "RMS" value of an equivalent sine wave. It has a 0 - 10 micro-inch scale, the readings on which must be multiplied by 10, when the attentuator located on the amplifier is set for 0.01 as was the case throughout these tests. The same values can be calculated mathematically from the graphs, but the meter is faster, very accurate, and may be sufficient alone if "hill and dale" chart profiles are not needed.

**** THE BRUSH SURFACE ANALYZER ****

TABLE II

Solution No.	Type Bath	COMPOSITION OF SOLUTIONS Addition Agents Conc. (g./l) Name	Wetting Agents Conc. (g./l) Name
1	Chloride	----	----
2	Chloride	2.0 Sodium o-Benzoyl Sulfimide	----
3	Chloride	2.0 Benzene Sulfonamide	----
4	Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	
5	Sulfate	----	----
6	Sulfate	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	----
7	Watts	----	----
8	Watts	----	1.0 Sodium Lauryl Sulfate
9	Watts	2.0 Sodium o-Benzoyl Sulfimide	----
10	Watts	2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate
11	Watts	2.0 Benzene Sulfonamide	----
12	Watts	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	----
13	Watts	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate
14	Watts	.1 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
15	Watts	.5 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
16	Watts	.9 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate

(Cont'd)

TABLE II (Cont'd.)

Solution No.	Type Bath	COMPOSITION OF SOLUTIONS Addition Agents Conc. (g./l) Name	Wetting Agents Conc. (g./l) Name
17	Watts	.1 Zinc Sulfate ($ZnSo_4.7H_2O$) 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate
18	Watts	.5 Zinc Sulfate ($ZnSo_4.7H_2O$) 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate
19	Watts	.9 Zinc Sulfate ($ZnSo_4.7H_2O$) 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate
20	Watts	.4 PQ	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
21	Watts	.6 PQ	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
22	Watts	.8 PQ	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
23	Watts	.4 PQ 2.0 Benzene Sulfonamide 2.0 Sodium o-Benzoyl Sulfimide	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
24	Watts	.6 PQ 2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
25	Watts	.8 PQ 2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
26	High Chloride	----	----

(Cont'd.)

TABLE II (Cont'd.)

Solution No.	Type Bath	COMPOSITION OF SOLUTIONS Addition Agents Conc. (g./l) Name	Wetting Agents Conc. (g./l) Name
27	High Chloride	----	1.0 Sodium Lauryl Sulfate
28	High Chloride	2.0 Sodium o-Benzoyl Sulfimide	----
29	High Chloride	2.0 Sodium o-Benzoyl Sulfimide	1.0 Sodium Lauryl Sulfate
30	High Chloride	2.0 Benzene Sulfonamide	----
31	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide	----
32	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide .1 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
33	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide .5 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
34	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide .9 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
35	High Chloride	2.0 Sodium o-Benzoyl Sulfimide .9 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate
36	High Chloride	.9 Zinc Sulfate ($ZnSo_4 \cdot 7H_2O$)	1.0 Sodium Lauryl Sulfate

(Cont'd.)

TABLE II (Cont'd.)

Solution No.	Type Bath	COMPOSITION OF SOLUTIONS Addition Agents Conc. (g./l) Name	Wetting Agents Conc. (g./l) Name
37	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide .4 PQ	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)
38	High Chloride	2.0 Sodium o-Benzoyl Sulfimide 2.0 Benzene Sulfonamide .6 PQ	1.0 Sodium Lauryl Sulfate 1.0 Sodium Fluoborate ($NaBF_4$)

PROCEDURE

The general scheme followed in this phase of the investigation was to obtain a profilograph and numerical value by means of the Brush Analyzer for buffed steel panels before and after nickel plating. The differences could then be utilized in comparing the "smoothing power" of the addition agents contained in the solutions of Table II.

To accomplish the above task, the Watts Type and High Chloride Baths described in Table I first had to be purified, as metallic and organic impurities in the bath could easily influence the results. This was accomplished by adding approximately ten liters of distilled water to a twenty liter glass cylinder and heating to 60°-70°C. by means of a circular glass steam coil immersed in the solution. The constituents (technical grade) necessary for fifteen liters of the bath were weighed out on a rough balance and added to the water. The salts were then allowed to dissolve and the cylinder was filled to the fifteen liter mark with distilled water. The pH of the bath was then adjusted electrometrically to approximately 5.5 by adding a slurry of nickel carbonate ($NiCO_3$) to the bath. The solution was then agitated by means of carbon filtered air and maintained at 60°-70°C. for 24 hours. This precipitated the iron as ferric hydroxide ($Fe(OH)_3$) and the aluminum as aluminum hydroxide ($Al(OH)_3$). The bath was then filtered through a Buechner Funnel previously prepared with a thick pad of asbestos. The filtered solution was then returned to

the same cylinder after cleaning and the pH adjusted to 3.0 by the addition of sulfuric acid (H_2SO_4) to the Watts Bath or hydrochloric acid (HCl) to the High Chloride Bath. A dummy corrugated steel cathode was then prepared from tin-can stock steel by bending a 24 x 10 inch strip into alternate 90° bends each $1\frac{1}{2}$ inch apart along the strip. The distance between the peaks of the bends was about two inches. After electrocleaning in an alkaline cleaner, pickling in 20% hydrochloric acid, and rinsing in running distilled water, the dummy cathode was suspended in the middle of the cylinder between two cold-rolled 99%+ nickel anodes. The monel metal hooks used for suspending the anodes were plated with a heavy deposit of nickel prior to using in order to avoid copper from contaminating the solution. A current density of 0.5 - 1.5 amperes per sq. ft. of apparent cathode surface (projected dimensions) was then applied for approximately 100 hours for the purpose of removing copper and other metallic impurities electrolytically from the solution. At the end of this period, a sample was removed from the bath, filtered and analyzed for copper colorimetrically by means of Levine and Serfass'[7] analysis procedure. If copper were still noticeably present, the electrolytic purification was continued until no significant amount of copper was detectable. The dummy cathode and nickel anodes were then removed, and about 6 g./l. of activated carbon was added to the bath for the purpose of removing organic impurities. Heating was continued, along with vigorous air agitation for about four hours or overnight. The solution was then filtered once again through a

Buechner funnel coated with asbestos, the pH adjusted to the desired value by means of a Beckman, Model G., pH meter, and stored in a twenty liter bottle.

The solutions used in the tests, as shown in Table II were prepared by dissolving the analytically weighed C. P. salts, with the exception of PQ, in one liter of the above purified nickel baths. PQ, the only semi-liquid addition agent used, was prepared for use daily by weighing out two grams in a weighing bottle and then dissolving in exactly twenty mls. of warm redistilled water. The desired amount of this addition agent was then added directly to the solution by means of a graduated pipette.

In each run, four 1 liter museum jars, containing the solutions under test were placed in a constant-temperature water bath maintained at 50°C. and a cold-rolled 99%+ nickel anode, encased in a white anode bag, was placed in one end of each jar. The 2" x 5" steel panels employed were polished with either a 120 or a 180 grain-polishing wheel. The 120 grain-polished panels were only used in a few of the solutions as they were too rough for real precise measurements. However, their value as panels were important because the irregularities were more pronounced on the graphs, thus permitting a more noticeable effect. The buffed panel was prepared for analysis and plating by scratching a line across the plate 2.9" from one end, thus making the effective plating area of the panel 1/25 ft.sq. The panel was then wiped free of grease with carbon tetrachloride (CCl_4), numbered, and reverse electrocleaned for two minutes in an alkaline

cleaner containing 21 g./l. of sodium hydroxide, 15 g./l. of sodium thiosulfate, 6 g./l. of sodium carbonate and 18 g./l. of sodium phosphate. It was then rinsed in cold running water, dipped for 10 seconds in 50% hydrochloric acid, rinsed again in cold water, distilled water, and wiped dry with a clean cheesecloth. The surface of the steel was then analyzed by means of the Brush Surface Analyzer at a point approximately one inch below the scratched line and one inch in from the outer edge. Only the meter reading was recorded at this point by taking the average of two readings in this immediate vicinity. Since the meter needle does not remain absolutely steady during the stylus' movement over the specimen, it was considered necessary to take three readings, viz., the maximum, minimum, and most constant or average needle deflection. The panel was then rinsed in distilled water, given a five second 50% hydrochloric acid dip to remove any dust or oil accumulated during the Brush Analyzer measurement, again rinsed in cold running water, distilled water, and secured in the cathode holder at the end of the cell opposite the anode so that the surface of the solution was at the scratch or level line. The cells were connected in series by means of insulated copper wire, and a current density of 40 amps per sq. ft. was applied for 44 minutes. Assuming a cathode efficiency of 95%, this would result in a deposit thickness of 0.0015 inch. Throughout each run, the solutions were moderately agitated at a constant rate by means of glass stirring rods connected to a pulley system operated by an electric motor. The panels were removed at the end of 44 minutes, rinsed in running

water, distilled water and dried with a clean cheesecloth. The unplated portion of the panel was then placed under the Brush Analyzer stylus, and moved around until a section was found that corresponded to the meter reading previously recorded. A profilograph was then made of this surface for a complete cycle of the stylus. The plated portion of the panel was then analyzed by placing the stylus on the surface as nearly as possible above the surface previously analyzed before plating. An oscillograph was then taken of this section and the meter reading recorded. The author did not make an oscillograph of the steel before plating because it would then have been impossible to place the profilograph of the steel and plate for any one panel side by side for ready comparison. The meter readings of the buffed steel for any one panel were very constant, and thus it is felt that no appreciable error was involved.

TABLE III

DATA OF THE SMOOTHING EFFECT ON STEEL (180-GRAIN-POLISH)

Current Density - 40 amps/Ft^2 Time 44 minutes

Plate thickness - .0015 inches pH = 4.0 (electrometric)

Panel No.	Solution No.	R.M.S. Microinches (Steel)			R.M.S. Microinches (Plate)			R.M.S. Microinches Difference		
		Min.	Av..	Max.	Min.	Av.	Max.	Min.	Av.	Max.
* 1	8	17	18	22	17	18	20	0	0	+2
2	15	12	13	16	12	13	15	0	0	1
3	16	11	12	13	8	10	12	3	2	1
4	17	12	13	15	10	11	12	2	2	3
5	18	13	14	15	10	11	11	3	3	4
6	19	11	12	13	8	9	10	3	3	3
7	10	9	10	11	8	8	9	1	2	2
8	13	9	9	10	8	8	9	1	1	1
9	20	12	13	14	7	8	10	5	5	4
10	21	15	16	17	7	8	9	8	8	8
11	22	12	13	14	6	7	8	6	6	6
12	23	12	13	14	6	7	8	6	6	6
13	24	16	16	18	6	7	8	10	9	10
14	25	14	15	17	6	7	8	8	8	9
**15	27	14	15	17	16	17	18	-2	-2	-1
16	29	9	9	9	7	8	9	2	1	0
17	35	8	9	10	6	7	8	2	2	2
18	34	17	18	19	12	12	15	5	6	4
19	33	12	13	15	6	8	9	6	5	6
20	37	12	13	14	6	7	8	6	6	6

* Standard Watts Bath

** Standard High Chloride Bath

TABLE IV

DATA OF THE SMOOTHING EFFECT ON STEEL (120-GRAIN-POLISH)

Current Density - 40 amps/Ft^2 Time 44 minutes

Thickness of Plate - .0015 inches pH - 4.0 (electrometric)

Panel No.	Solution No.	R.M.S. Microinches (Steel)			R.M.S. Microinches (Plate)			R.M.S. Microinches Difference		
		Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.
24	8	56	60	63	54	58	66	2	2	3
25	16	54	58	64	50	52	53	4	6	11
26	19	48	53	56	42	46	49	6	7	7
27	20	62	64	68	32	35	46	30	29	22
28	21	56	63	68	24	26	33	32	37	35
29	22	56	63	66	30	32	44	26	31	22
30	23	60	64	72	28	31	34	32	33	38
31	24	59	64	72	16	18	21	43	46	51
32	25	52	59	60	20	22	30	32	37	30
33	27	60	64	66	56	64	68	4	0	-2
34	34	60	62	64	44	49	51	16	13	13
35	37	40	45	50	24	26	28	16	19	22

TABLE V

DATA ON THE EFFECT OF pH ON SMOOTHNESS MEASUREMENTS STEEL (180-GRAIN-POLISH)

Current Density - 40 amps/Ft^2 Temperature - 50oC.

Panel No.	Solution No.	pH	R.M.S. Microinches (Steel)			R.M.S. Microinches (Plate)			R.M.S. Microinches Difference		
			Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.
1	8	4.0	17	17	22	17	18	20	0	-1	+2
21	8	3.0	9	9	9	9	9	9	0	0	0
3	16	4.0	11	12	13	8	10	13	3	2	0
22	16	3.0	9	9	10	10	10	12	-1	-1	-2
6	19	4.0	12	12	13	8	9	10	3	3	3
23	19	3.0	8	8	9	5	6	7	3	2	2
15	27	4.0	14	15	17	16	17	18	-2	-2	-1
36	27	3.0	9	9	10	12	12	13	-3	-3	-3
17	35	4.0	8	9	10	6	7	8	2	2	2
37	35	3.0	9	9	9	6	7	7	3	2	2
18	34	4.0	17	18	19	12	12	15	5	6	4
38	34	3.0	11	12	12	7	7	9	4	5	3

TABLE VI

AVERAGE PERCENT IMPROVEMENT AND APPEARANCE OF SURFACE STEEL
(180 GRAIN-POLISH)

Panel No.	Solution No.	Av. Percent Improvement	Appearance
1	8	0	Grey
2	15	0	Grey
3	16	16.7	Grey
4	17	15.4	Cloudy
5	18	21.4	Cloudy
6	19	25.0	Cloudy
7	10	20.0	Cloudy
8	13	11.1	Cloudy
9	20	38.4	Cloudy-Lustrous
10	21	50.0	Lustrous
11	22	46.0	Slightly cloudy-lustrous
12	23	46.0	Lustrous
13	24	56.5	Lustrous
14	25	53.5	Lustrous
15	27	-13.0	Dark grey
16	29	11.0	Cloudy-Lustrous
17	35	22.0	Slightly cloudy-lustrous
18	34	33.3	Cloudy-Lustrous
19	33	38.4	Slightly cloudy-lustrous
20	37	46.3	Lustrous

TABLE VII

AVERAGE PERCENT IMPROVEMENT AND APPEARANCE OF SURFACE STEEL (120 GRAIN-POLISH)

Panel No.	Solution No.	Percent Improvement	Appearance
24	8	3.3	Light grey
25	16	10.4	Light grey
26	19	13.2	Cloudy, trace of luster
27	20	45.5	Slightly cloudy, lustrous
28	21	58.7	Slightly cloudy, lustrous
29	22	49.2	Slightly cloudy, lustrous
30	23	51.7	Slightly cloudy, lustrous
31	24	71.9	Lustrous
32	25	62.9	Lustrous
33	27	0	Dark grey
34	34	21.0	Cloudy, slightly lustrous
35	37	42.3	Slightly cloudy, lustrous

TABLE VIII

EFFECT OF pH ON AVERAGE PERCENT IMPROVEMENT AND APPEARANCE OF SURFACE STEEL (180 GRAIN POLISH) pH = 3.0 or 4.0

Panel No.	Solution No.	pH	Percent Improvement	Appearance
1	8	4.0	0	Grey
21	8	3.0	0	Grey
3	16	4.0	16.7	Grey
22	16	3.0	-11.1	Grey
6	19	4.0	25.0	Cloudy
23	19	3.0	25.0	Cloudy, slightly lustrous
15	27	4.0	-13.0	Dark Grey
36	27	3.0	-33.4	Dark Grey
17	35	4.0	22.2	Slightly cloudy, lustrous
37	35	3.0	22.2	Slightly cloudy, lustrous
18	34	4.0	33.2	Cloudy lustrous
38	34	3.0	41.5	Slightly cloudy, lustrous

TABLE IX

THE EFFECT OF THE SUBSURFACE ON "SMOOTHING POWER"		
Solution No.	Percent Improvement (120 Grain-polish)	Percent Improvement (180 Grain-polish)
8	3.3	0
16	10.4	16.7
19	13.2	25.0
20	45.5	38.4
21	58.7	50.0
22	49.2	46.0
23	51.7	46.0
24	71.9	56.5
25	62.9	53.5
27	0	-13.0
34	21.0	33.0
37	42.3	46.3

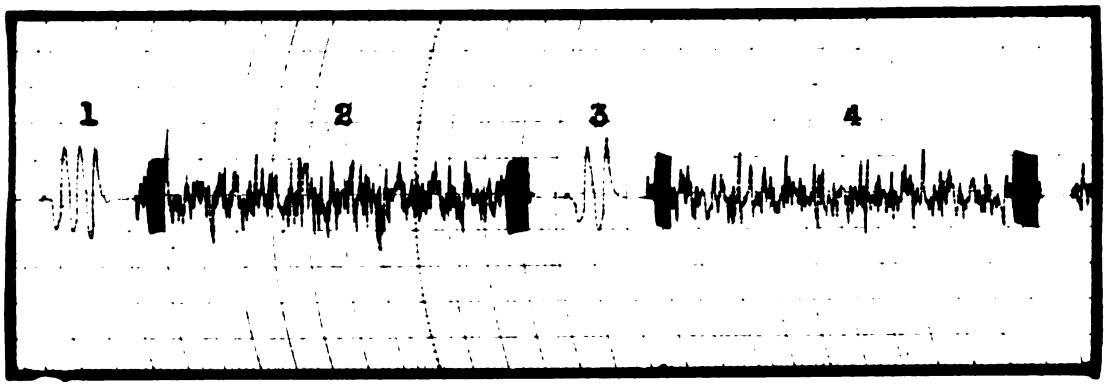


Fig.1.-Profilograph of Panel 1. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4.Plate

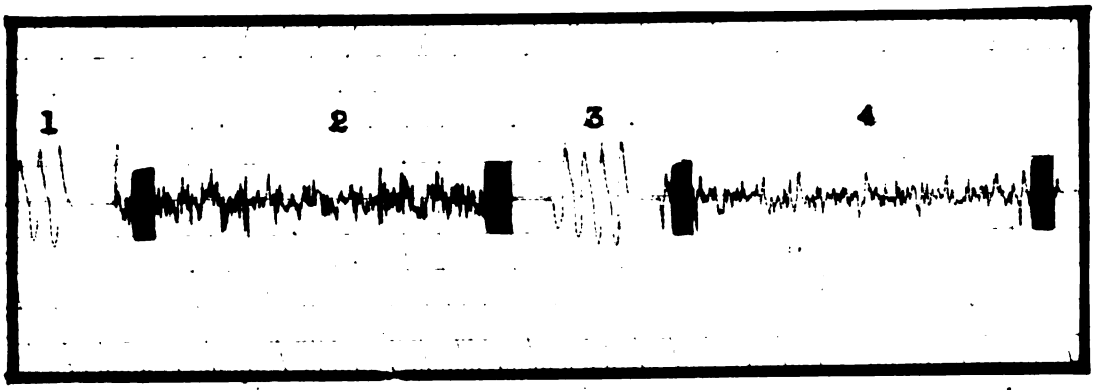


Fig.2.-Profilograph of Panel 2. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

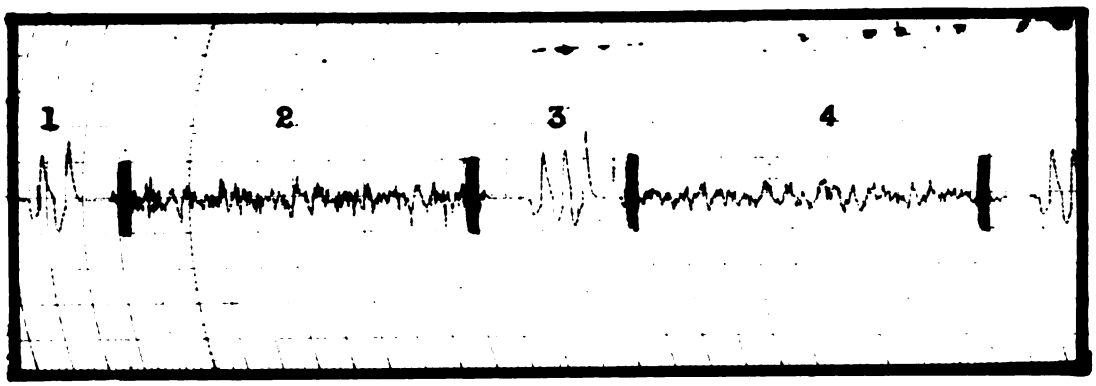


Fig.3.-Profilograph of Panel 3. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

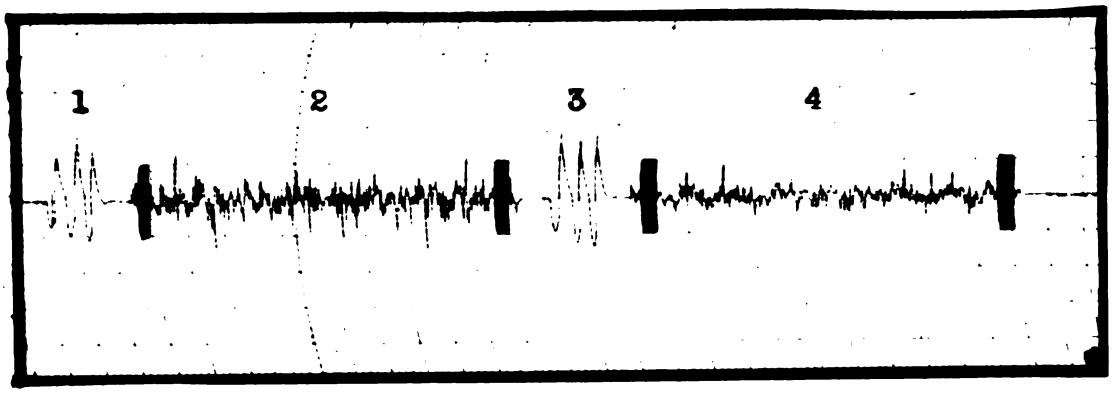


Fig.4.-Profilograph of Panel 4. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

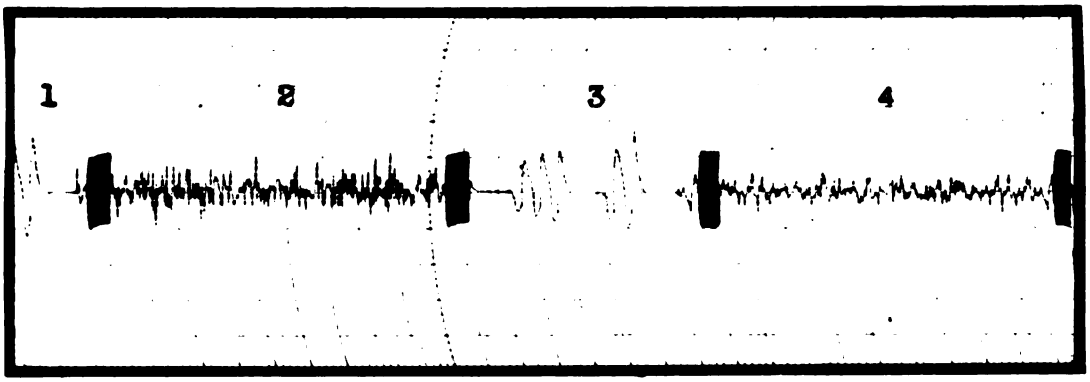


Fig.5.-Profilograph of Panel 5. Curves: 1.Calibration 2. Steel-180 grain polish 3.Calibration 4. Plate

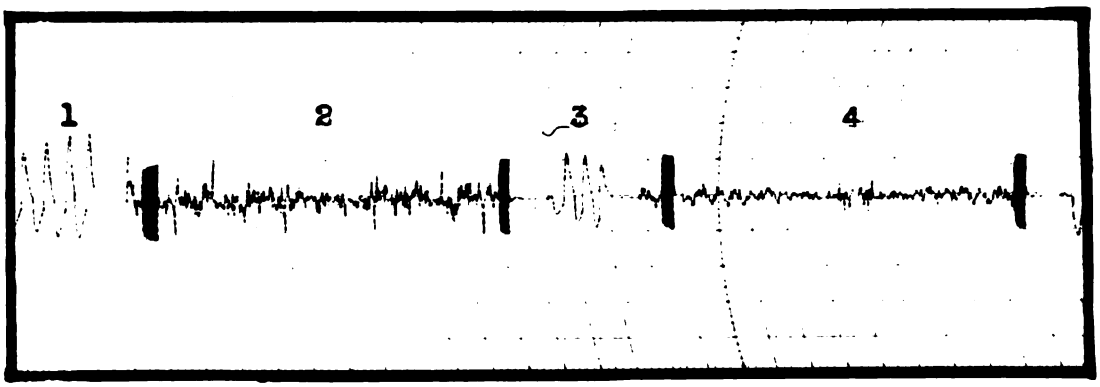


Fig.6.-Profilograph of Panel 6. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

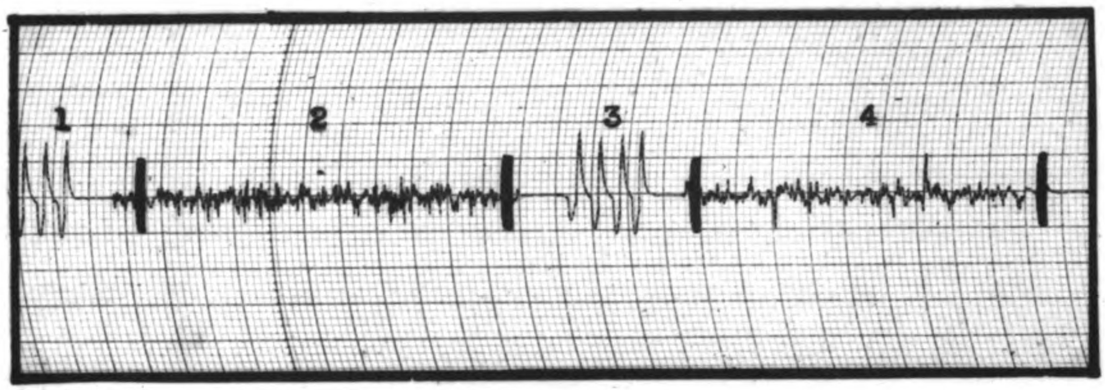


Fig.7.-Profilograph of Panel 7. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

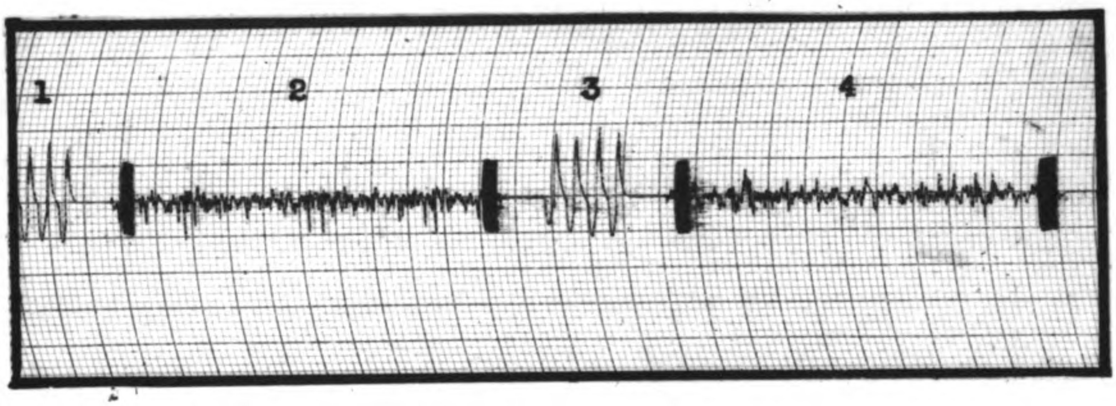
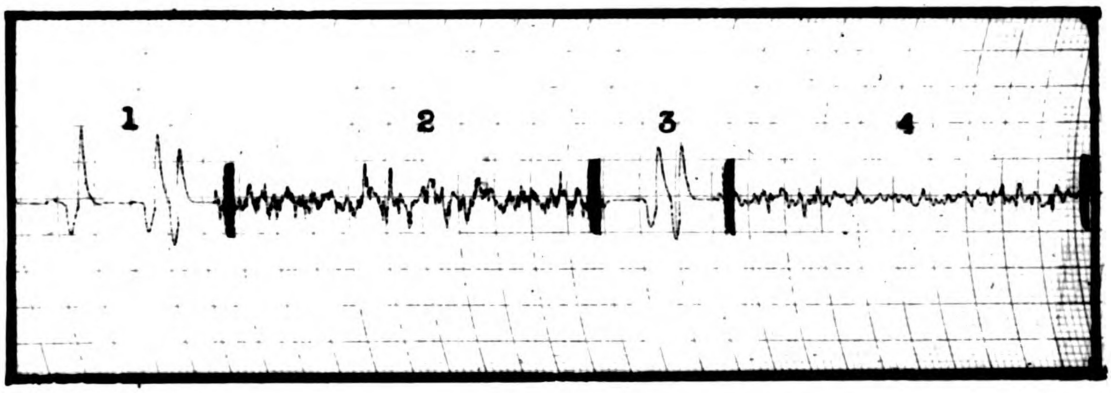


Fig.8.-Profilograph of Panel 8. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate



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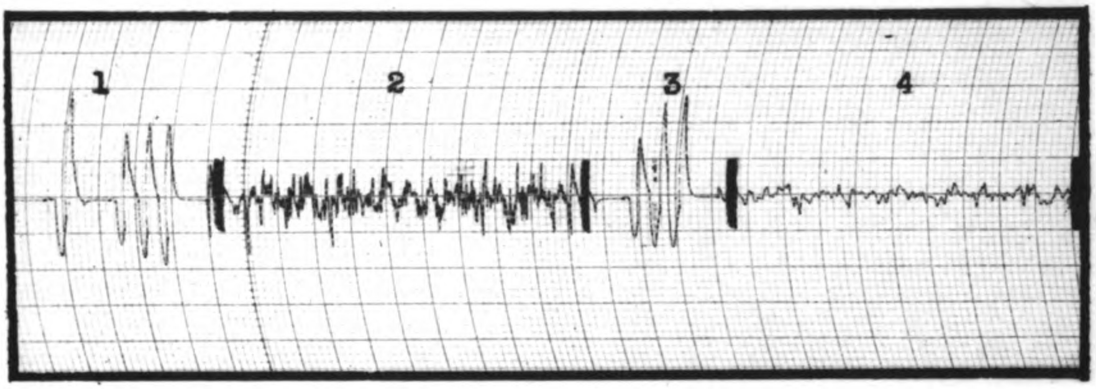

Fig.10.-Profilograph of Panel 10. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

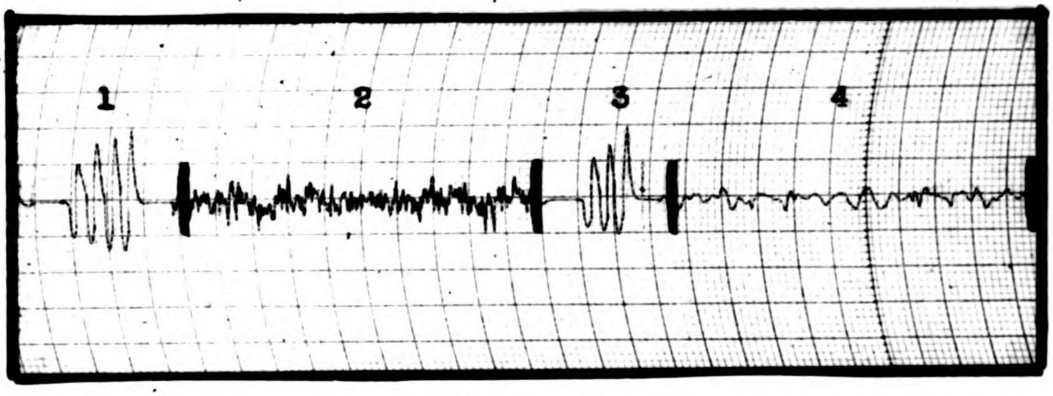

Fig.11.-Profilograph of Panel 11. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4.Plate

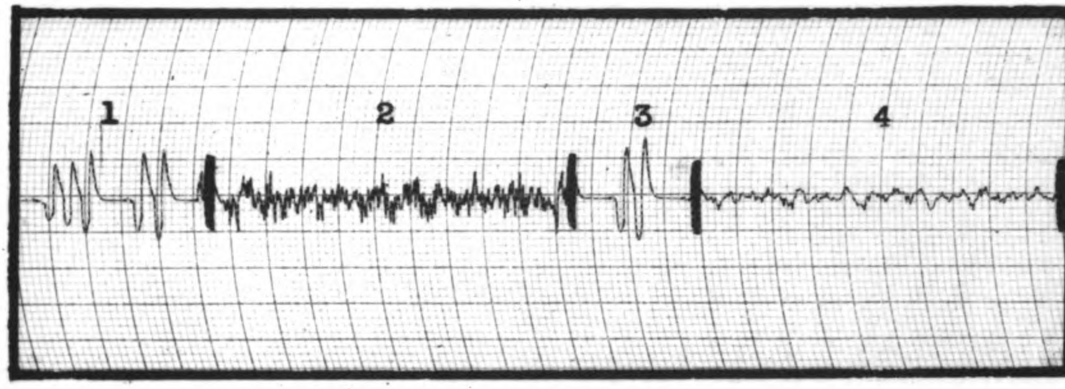

Fig.12.-Profilograph of Panel 12. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

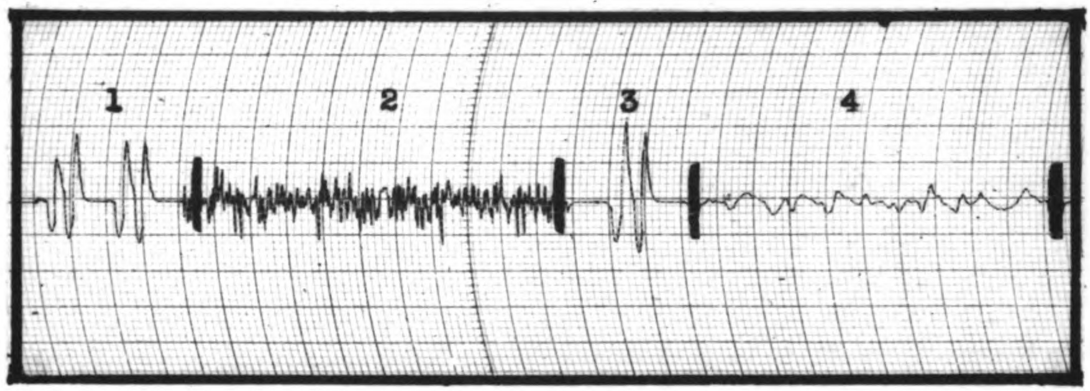

Fig.13.-Profilograph of Panel 13. Curves: 1. Calibration 2. Steel-180 grain polish 3.Calibration 4. Plate

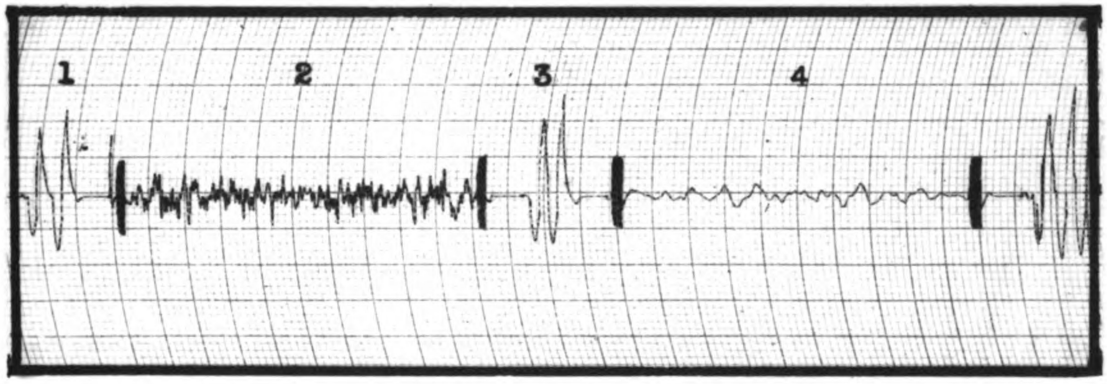

Fig.14.-Profilograph of Panel 14. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

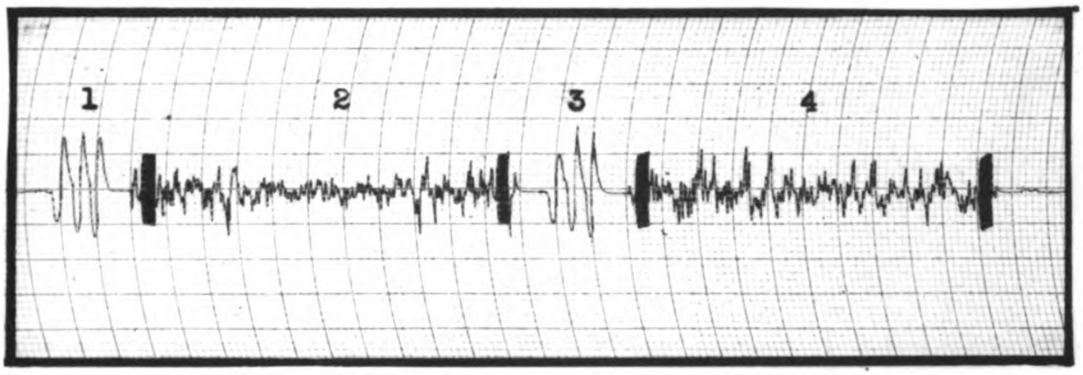

Fig.15.-Profilograph of Panel 15. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

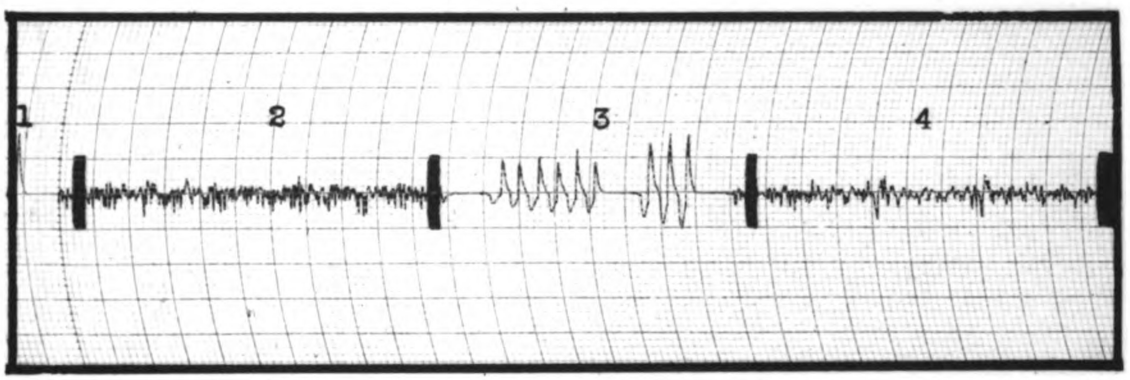

Fig.16.-Profilograph of Panel 16. Curves: 1. Calibration 2.Steel-180 grain polish 3. Calibration 4. Plate

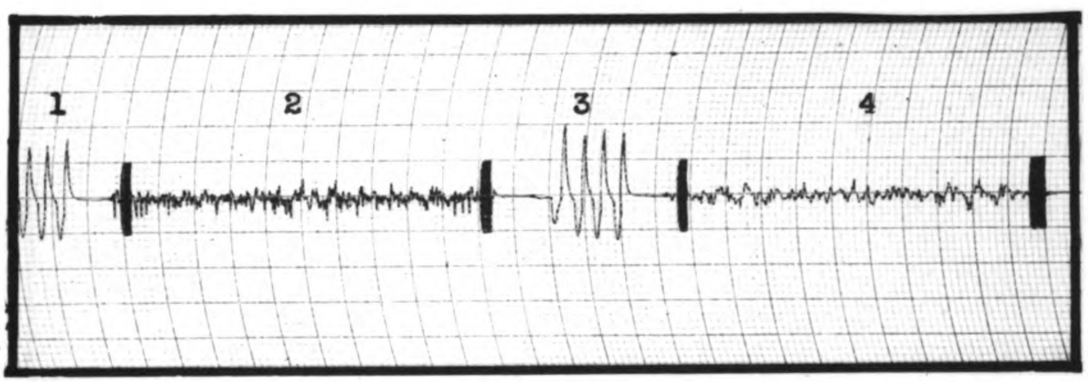

Fig.17.-Profilograph of Panel 17. Curves 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

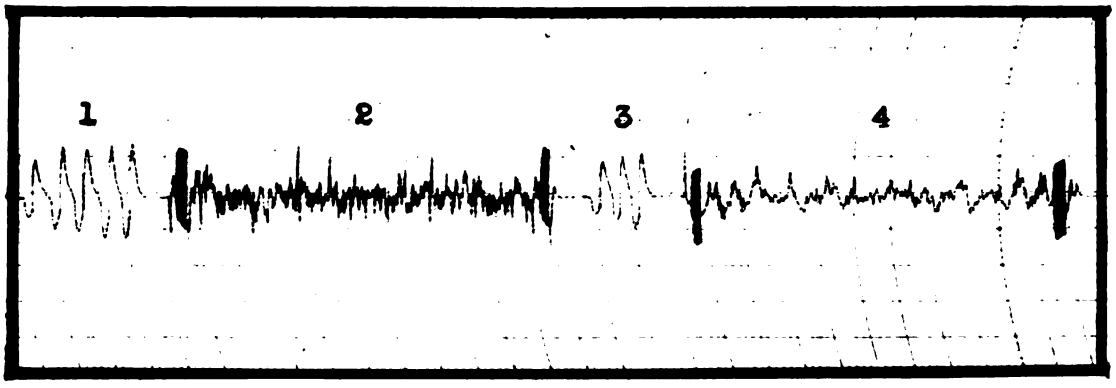

Fig.18.-Profilograph of Panel 18. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

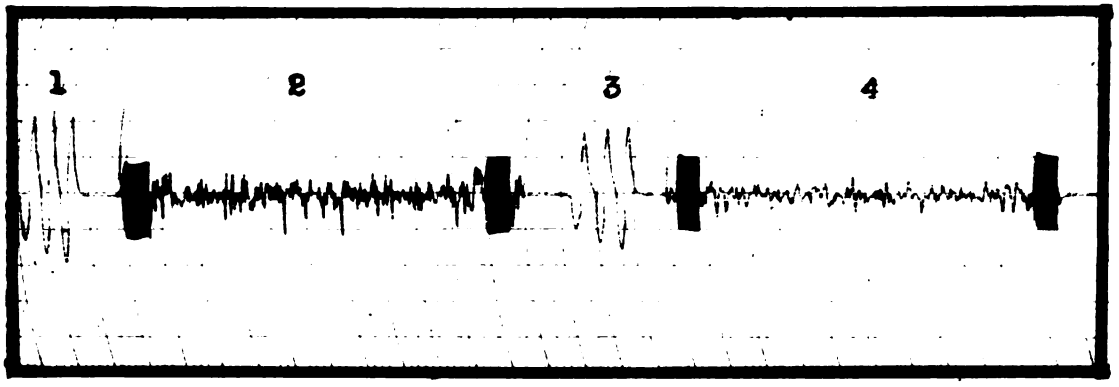

Fig.19.-Profilograph of Panel 19. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

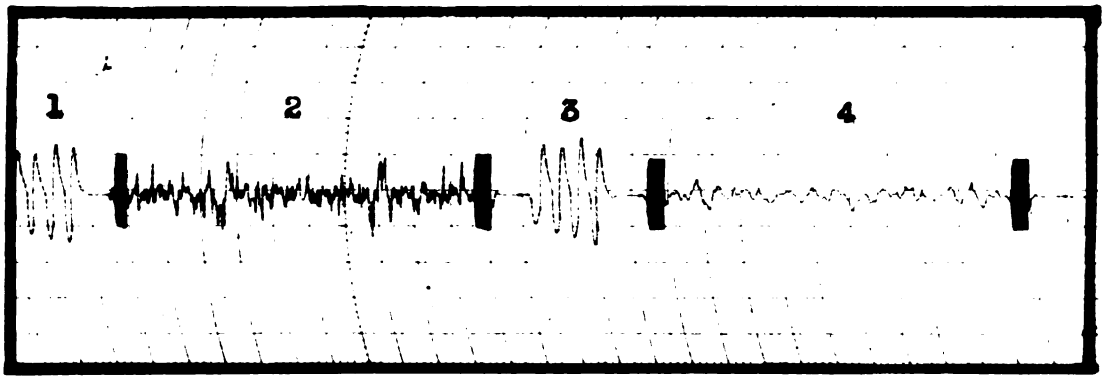

Fig.20.-Profilograph of Panel 20. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

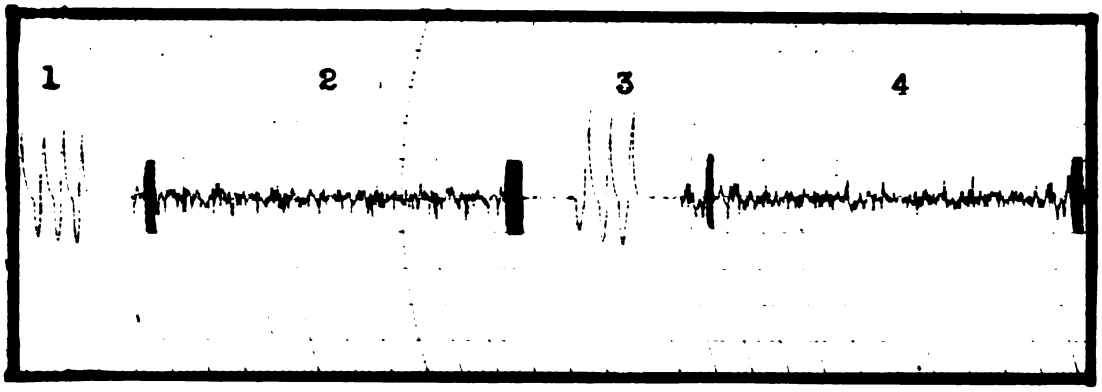

Fig.21.-Profilograph of Panel 21. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

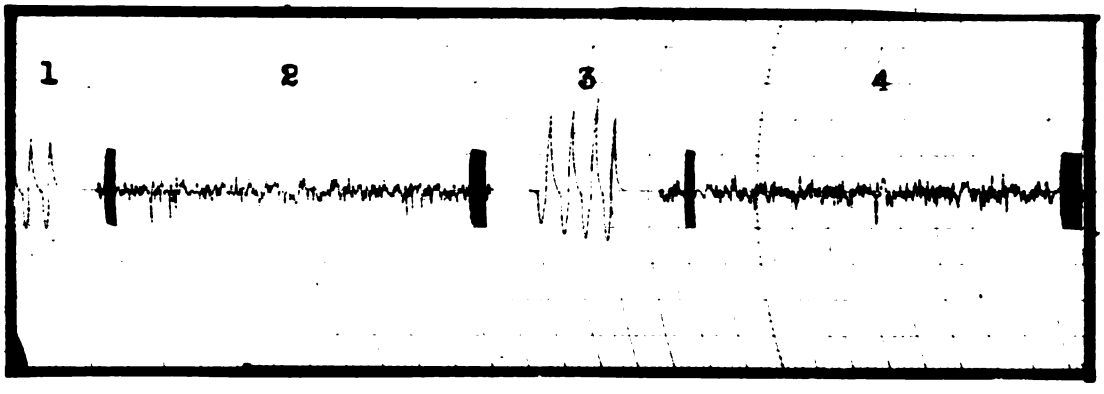

Fig.22.-Profilograph of Panel 22. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

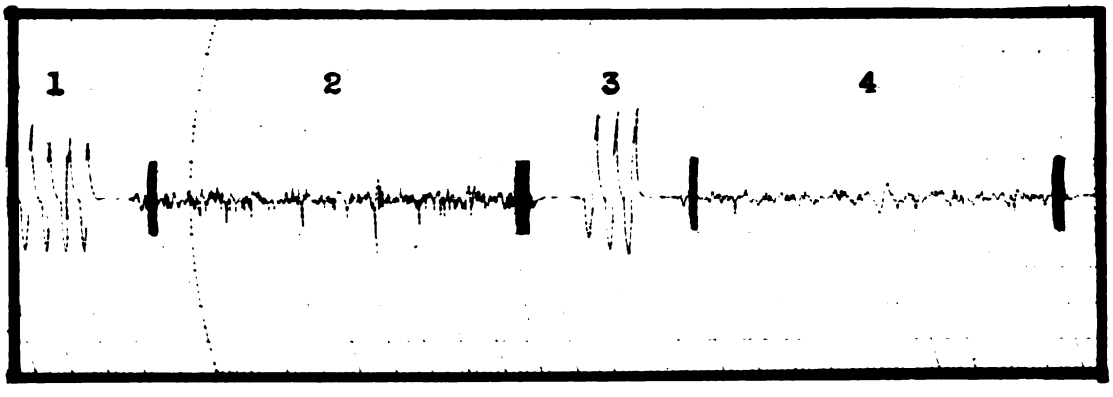

Fig.23.-Profilograph of Panel 23. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

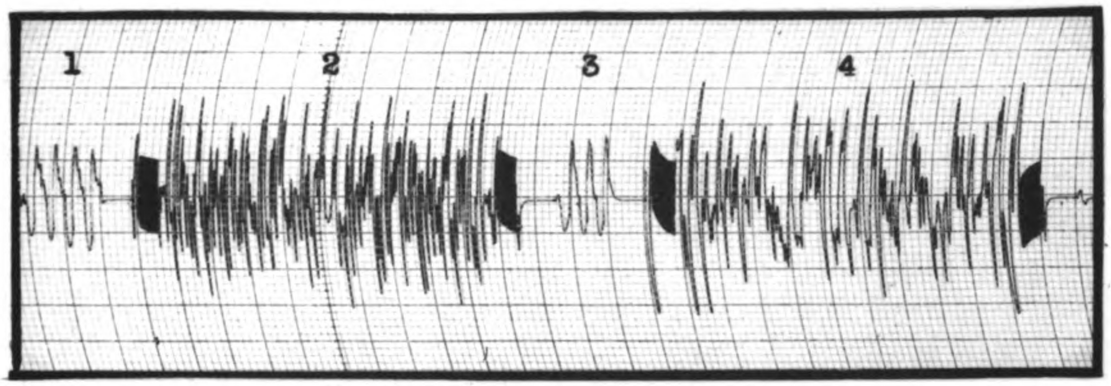

Fig.24.-Profilograph of Panel 24. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

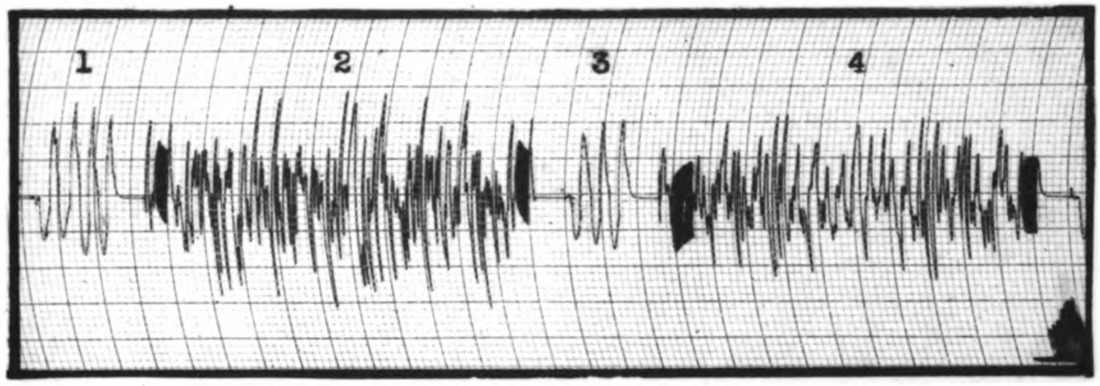

Fig. 25.-Profilograph of Panel 25. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

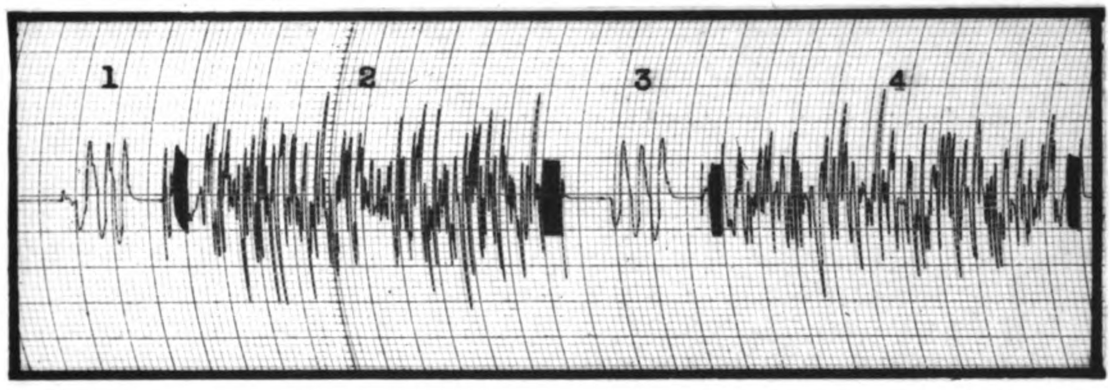

Fig.26.-Profilograph of Panel 26. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

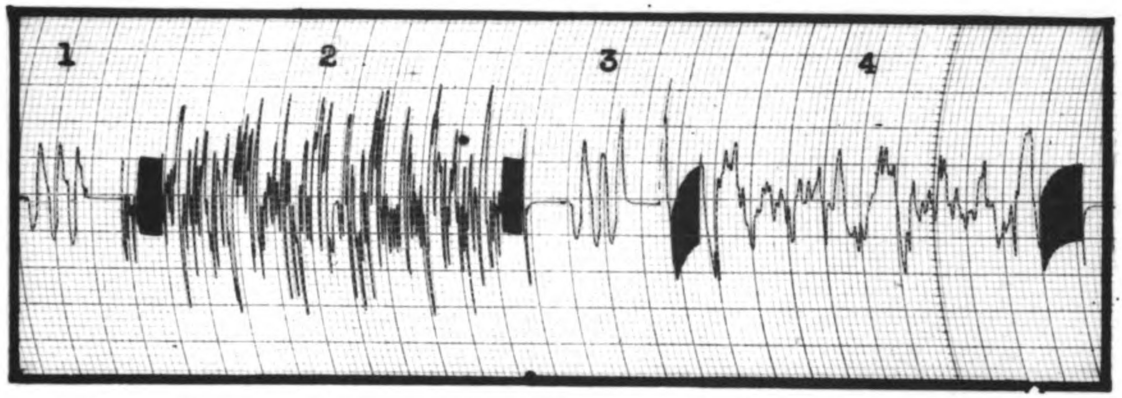

Fig.27.-Profilograph of Panel 27. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

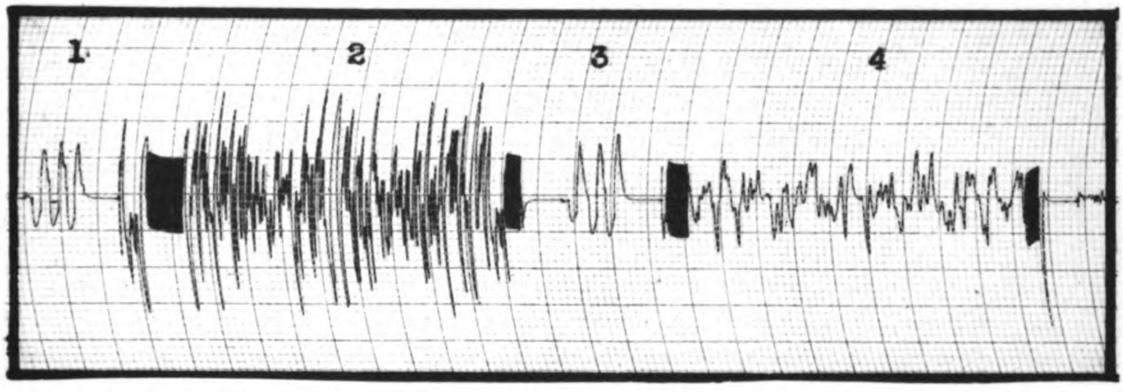

Fig.28.-Profilograph of Panel 28. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

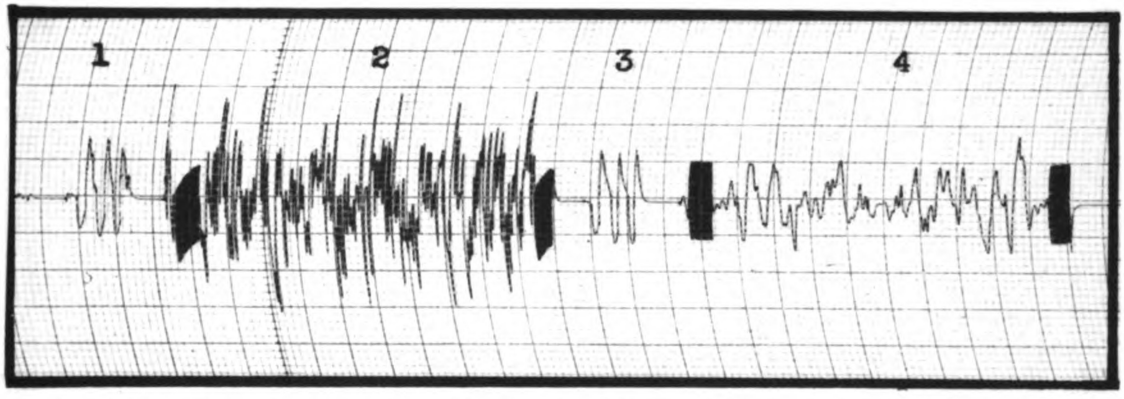

Fig.29.-Profilograph of Panel 29. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

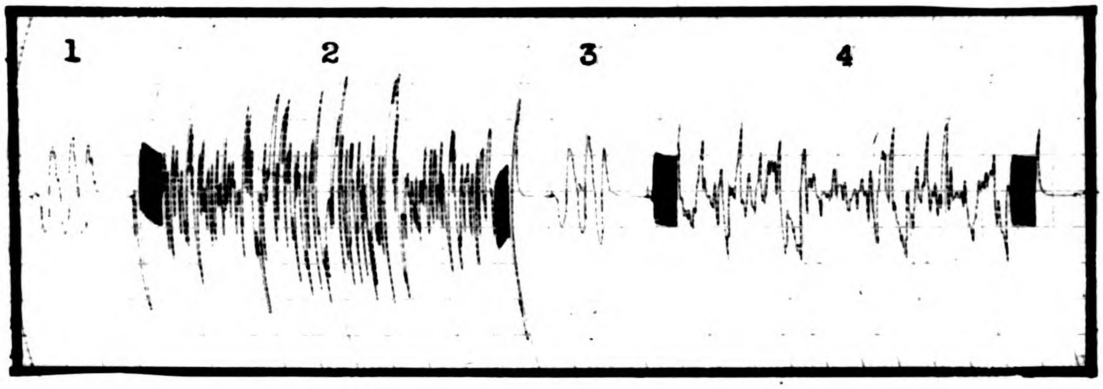

Fig.30.-Profilograph of Panel 30. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

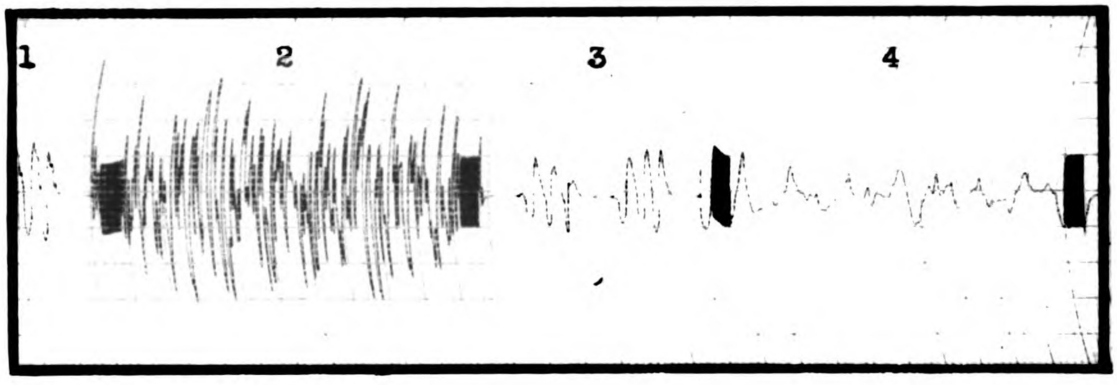

Fig.31.-Profilograph of Panel 31. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

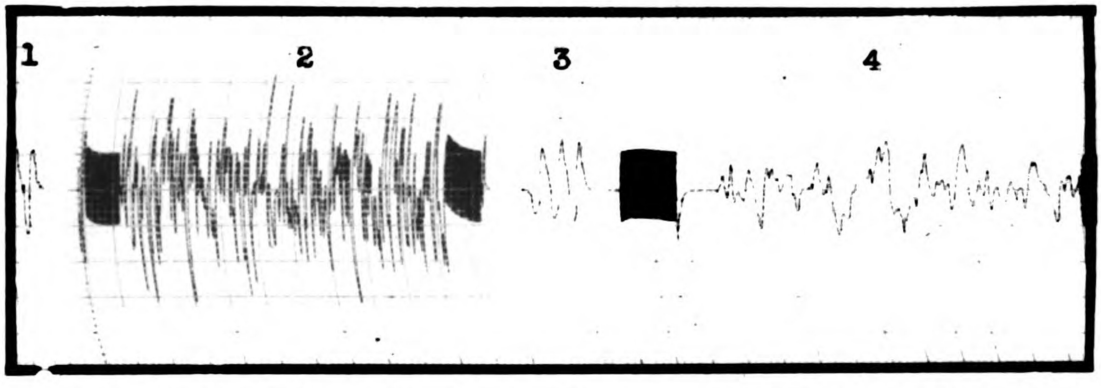

Fig.32.-Profilograph of Panel 32. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

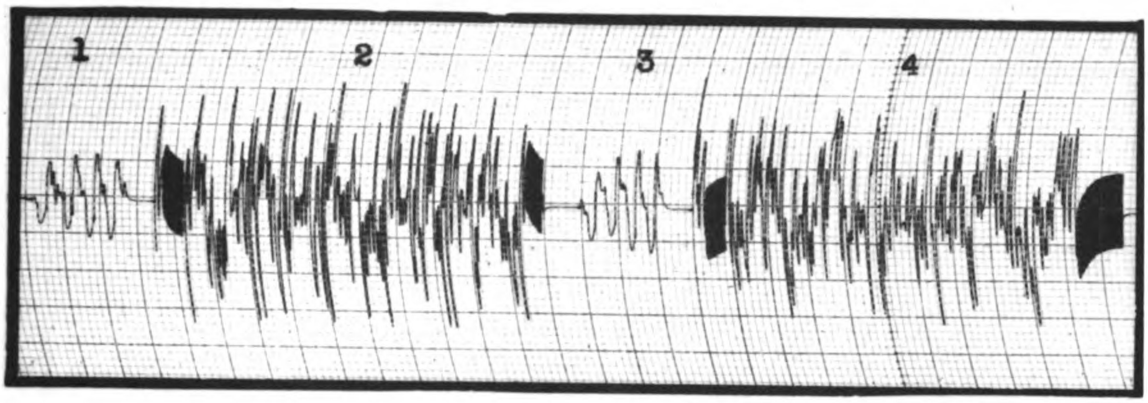

Fig.33.-Profilograph of Panel 33. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

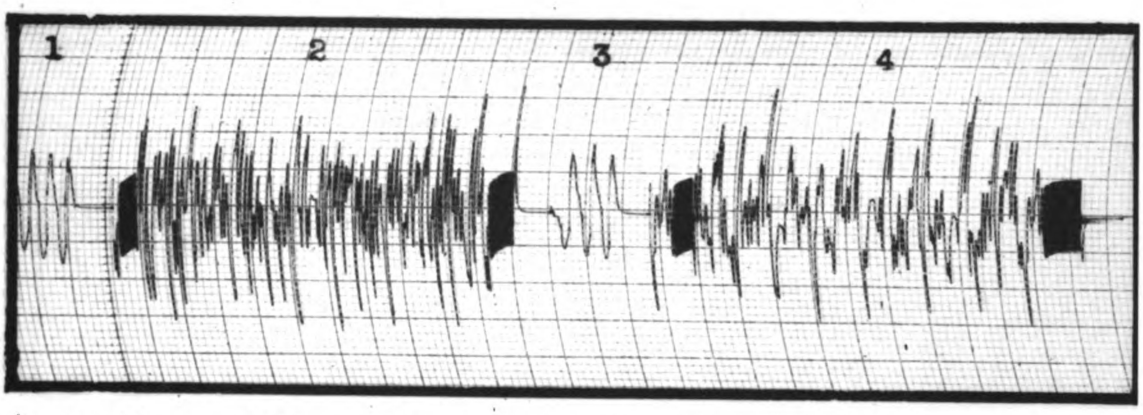

Fig.34.-Profilograph of Panel 34. Curves: 1. Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

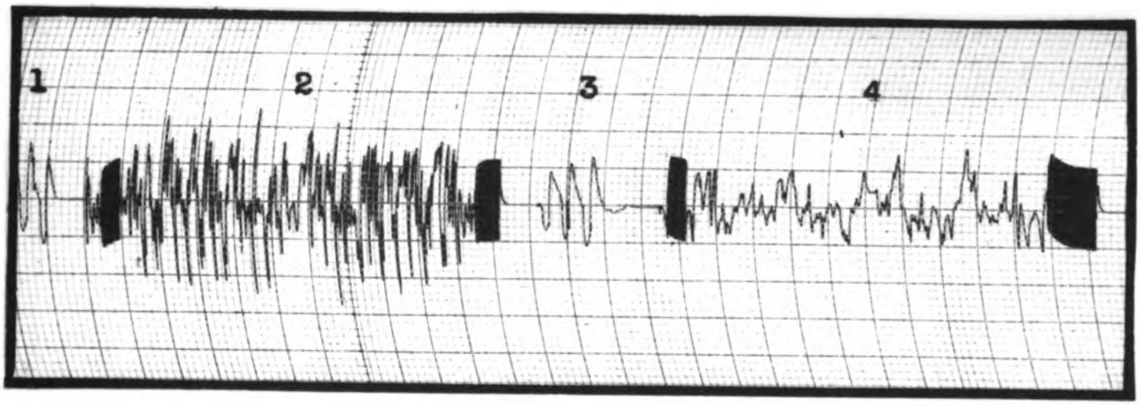

Fig.35.-Profilograph of Panel 35. Curves: 1.Calibration 2. Steel-120 grain polish 3. Calibration 4. Plate

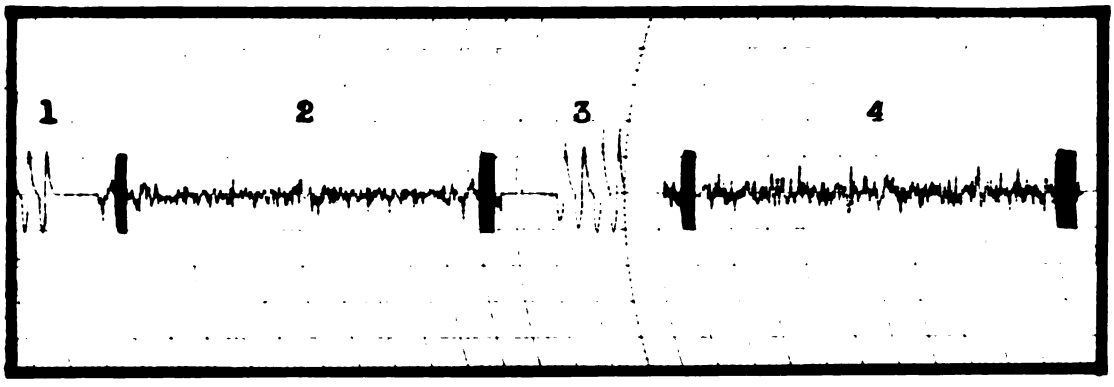

Fig.36.-Profilograph of Panel 36. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

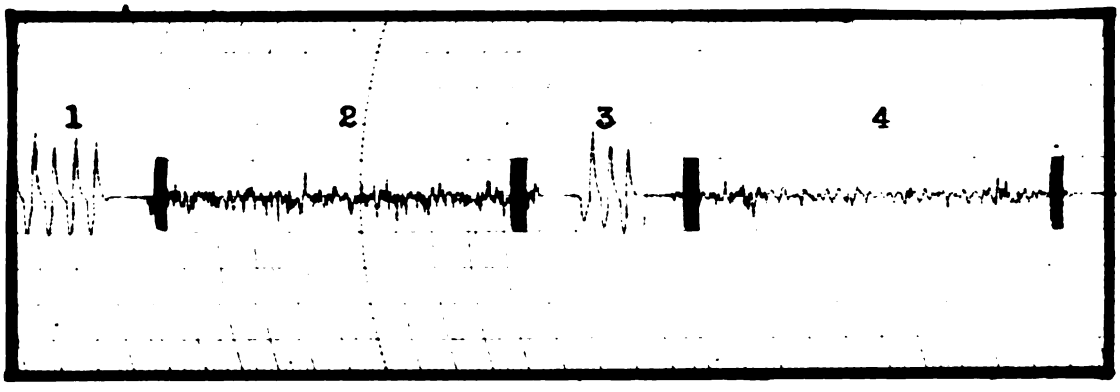

Fig37.-Profilograph of Panel 37. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

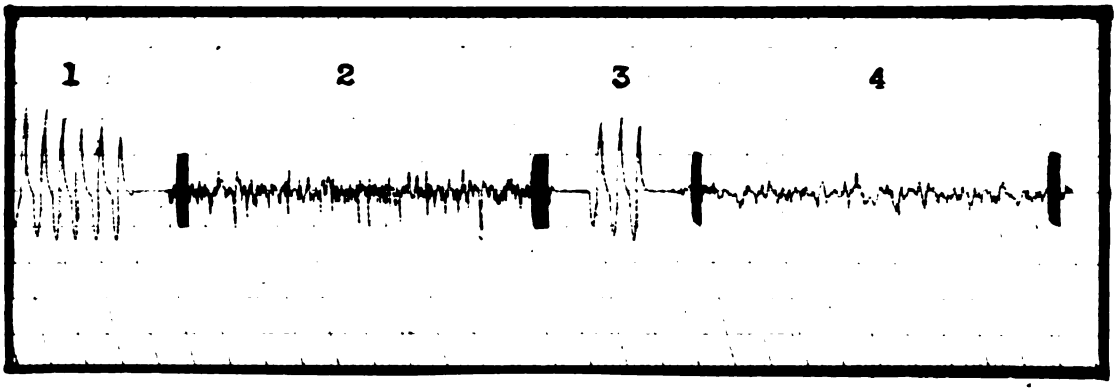

Fig.38.-Profilograph of Panel 38. Curves: 1. Calibration 2. Steel-180 grain polish 3. Calibration 4. Plate

DISCUSSION OF RESULTS

PART I

Data and graphs for this phrase of the investigation are found in Tables III-V, and in Figs. 1-38 inclusive. The author has also prepared Tables VI-IX inclusive for the purpose of facilitating a clearer and more understandable comparison of the results. Throughout this investigation, solution 8 consisting of the Watts Type Bath plus 1 g./l. of sodium lauryl sulfate, and solution 27, consisting of the High Chloride Bath plus 1 g./l. of sodium lauryl sulfate were considered as the standard solutions, and thus the effect of addition agents will be discussed in reference to these baths.

Watts Type Bath - (180 grain-polished panels)

The standard bath, solution 8, has on the average, no noticeable effect on the surface at a pH of 4.0, as shown by Tables III and VI. Fig. 1 indicates, however, that some of the rougher surface irregularities are improved. Lowering the pH to 3.0 has little if any significance. The addition of 0.5 g./l. or 0.9 g./l. of zinc sulfate ($ZnSO_4.7H_2O$) to the standard bath has no affect on the grey appearance of the plate. Figs. 2 and 3, however, both show a definite decrease and spreading out of roughness, with 0.9 g./l. of zinc sulfate being the most beneficial. Lowering the pH to 3.0 has a decided detrimental effect as can be readily seen by comparing the profilographs of Figs. 3 and 22. Solution 17, consisting of benzene sulfonamide and 0.1 g./l. of zinc sulfate in the standard bath,

produced a plate improvement approximately the same as that obtained with solution 16, containing a higher percentage of zinc but no benzene sulfonamide. Thus the lowered effect of the zinc concentration was approximately made up by the addition of the benzene sulfonamide. In addition, it is noted that although the average effect of solutions 16 and 17 are the same, the latter produces a more lustrous panel. This discrepancy can be explained, however, by noting that solution 17 is more effective in smoothing over the rougher irregularities. The addition of benzene sulfonamide to 0.5 g./l. of zinc sulfate (solution 18) and to 0.9 g./l. of zinc sulfate (solution 19) improves the plate smoothness directly with an increase in zinc concentration as can be noted in Figs. 5 and 6. An inspection of Table VI also shows that each increase of 0.4 g./l. of zinc sulfate increases the average percent improvement about 5% when benzene sulfonamide is present. Lowering the pH from 4.0 to 3.0 had no effect on solution 19. Benzene sulfonamide, by itself, appears to have a beneficial effect on the Watts Bath as Table VI indicates an improvement of 20% for solution 10 over solution 8. Fig. 7 substantiates this improvement as does also the increased luster of the panel. When sodium o-Benzoyl sulfimide is added along with benzene sulfonamide to the Watts Bath as in solution 13, however, the percent improvement is lowered, suggesting that the former addition agent hinders to a slight extent the beneficial effects of benzene sulfonamide. Solutions 20, 21, and 22, containing 0.4 g./l., 0.6 g./l., and 0.8 g./l. of

PQ - 1 g./l. of sodium fluoborate ($NaBF_4$) respectively in the standard solution have very decided beneficial effects on smoothing power. This is readily apparent by noting the marked improvements in the appearance of the plates, as well as the improved profilographs in Fig. 9 (solution 20), Fig. 10 (solution 21) and Fig. 11 (solution 22). This addition agent of class II displayed in all concentrations studied a decided ability to remove or round off surface irregularities. Table VI, shows that solution 21 (containing PQ in a concentration of 0.6 g./l.) is the most effective with an improvement of 50%, and this indicates that PQ does not increase its effectiveness directly with an increase of concentration as was apparent with the zinc addition agent. Fig. 12 (solution 23), Fig. 13 (solution 24) and Fig. 14 (solution 25) show definitely that the addition of benzene sulfonamide and o-benzoyl sulfimide to PQ enhances the effect of the latter addition agent. Here again the solution containing the 0.6 g./l. of PQ (solution 13) shows the most improvement. Inspection of Table VI, shows a rather interesting observation in that the solutions containing 0.6 g./l. of PQ improved the surface approximately 11% over those with 0.4 g./l. PQ and approximately 3 - 4% over those containing 0.8 g./l. of PQ, with or without the presence of the Class I addition agents. These latter compounds, however, increased the hiding power of all concentrations of PQ by about 7%. A comparison of solutions 22 and 23 in Table VI also suggests another interesting fact. Solution 23, containing 0.4 g./l. PQ plus both Class I addition agents,

has the same percent improvement as solution 22, containing 0.8 g./l. of PQ and no Class I compounds. Thus it is apparent that to some extent Class I addition agents can make up for a loss of effectiveness in PQ due to concentration just as they were able to do with zinc sulfate.

High Chloride Bath - (180 grain-polished panels)

Solution 27, the standard High Chloride Bath, has a decided harmful effect at both a pH of 4.0 and a pH of 3.0. This is easily attested to by observing Figs. 15 and 36 and Tables V and VIII. The lower pH is decidedly more harmful, although in appearance both plates are a dark grey without any noticeable differences. O-Benzoyl sulfimide added to the standard bath, as in solution 29, improves the steel surface about 11% and the effect of the standard solution by about 25%. This improvement, however, is still insufficient to improve the appearance of the plate. By adding 0.9 g./l. of $ZnSO_4$ to the o-benzoyl sulfimide, as in solution 35, the effective smoothing power is increased another 11% at each pH. Here again, as in the Watts Bath, the Class I addition agents appear to have a greater beneficial effect at the lower pH. This solution also improved the appearance of the plate from a dark grey to a slightly-cloudy lustrous finish. In solution 34, the addition of benzene sulfonamide to solution 35, further improves the smoothing effect at either pH, being somewhat better at a pH of 3.0. This can be readily seen by inspecting Table VIII and Figs. 17 and 18. A comparison of panel 18 (solution 34) with panel 17 (solution 35),

however, brings forth another interesting point, that must necessarily be considered in comparing the appearance of surfaces. Solution 34 has more of a beneficial effect than solution 35, and yet panel 17 is more lustrous than panel 18. This is readily accounted for by the fact that the subsurface of panel 18 is rougher than panel 17 as noted in Table III. The increased smoothing effect of solution 34 has decreased this discrepency somewhat but panel 18 is still rougher after plating than is panel 17. This fact definitely indicates the importance of considering the subsurface before comparing the relative merits of different solutions as to their smoothing ability. Solution 33, containing 0.5 g./l. of zinc sulfate plus both Class I addition agent in the standard bath, is slightly more effective than solution 34 containing 0.9 g./l. of zinc sulfate plus the Class I compounds. This is directly opposite to the effect of zinc concentration in the standard Watts Bath. Solution 37, again attests to the effectiveness of PQ as a smoothing agent. Fig. 20 shows a considerable leveling effect, and the 46% improvement over the steel surface is sufficient to produce a lustrous mirror finish. PQ, in this standard High Chloride Bath, as in the Watts, is by far the most effective addition agent tested.

Watts Type Bath - (120 grain-polished panels)

As was previously explained in the introduction, the 120 grain-polished panels are rougher than the usual work to be commercially plated. However, as can be seen from viewing Figs. 24 - 35 inclusive,

the improvements of surface finish by the various solutions, is much more readily apparent. Furthermore, the relative effectiveness of addition agents in smoothing over the irregularities of these panels, can be used in conjunction with results obtained for the same compounds on the 180 grain-polished panels. Table VII shows the average percent improvement and the appearance of the surface after plating and Table IX makes it possible to more readily compare the effects of the same solution on the two differently polished panels.

The standard Watts Bath (solution 8) shows an insignificant 3% improvement, and little if any beneficial effect on the profilograph in Fig. 24. Thus the effect on either panel is approximately the same, as shown in Table IX. The addition of 0.9 g./l. of zinc sulfate to the standard bath increased the improvement to 10.5%, and this difference of about 7 - 8% was sufficient to show a marked improvement in the profilograph of Fig. 25. The percent improvement is slightly less than for the smoother panel. The addition of benzene sulfonimide to the 0.9 g./l. of zinc sulfate, as in solution 19, improved the surface another 3% and produced a somewhat lustrous finish. An inspection of Figs. 27, 28, and 29 show the remarkable smoothing power of the PQ solutions 20, 21, and 22. The high percent improvements in Table VII further collaborate the exceptional hiding power possessed by this addition agent. A concentration of 0.6 g./l. is again found to produce the maximum results, and it is also noted in Table IX that all concentrations of PQ show more of an improvement on the 120 grain-polished panels than on the 180 grain-polished panels.

The beneficial effect of both Class I addition agents on PQ is again illustrated on these panels, for solutions 23, 24, 25 produced an additional 6 - 13% improvement over the corresponding solutions containing no Class I compounds. This improvement in surface smoothness was sufficient to produce a highly lustrous panel. Figs. 30, 31, and 32 show surfaces comparatively free of roughness. The addition agents have removed most of the surface irregularities and have rounded off the more pronounced peaks.

High Chloride Bath - (120 grain-polished panels)

The High Chloride Bath (solution 27) produced no apparent change in the smoothness of the steel panel, in contrast to the 13% harmful effect on the smoother panels. 0.9 g./l. of zinc sulfate in the standard solution improved the smoothness about 21% and spread out the surface imperfections to some extent in curve (2), Fig. 34. Solution 37, containing 0.4 g./l. of PQ plus both Class I compounds again produced the smoothest plate and brightest finish. Fig. 35 shows a considerable "hiding effect", although it is further noted that PQ is somewhat less effective in the High Chloride Bath than in the Watts Bath.

CONCLUSIONS

The author feels confident that the foregoing data and discussion attests to the validity of the following conclusions.

1. Allyl-chloracetate quaternary of pyridine (PQ) has by far the greatest "smoothing power" of the addition agents investigated, and is most effective in a concentration of 0.6 g./l.
2. PQ is somewhat more effective in the Watts than in the High Chloride Bath.
3. Benzene sulfonamide and sodium o-benzoyl sulfimide enhance the action of PQ.
4. Zinc produces a slight smoothing effect as does benzene sulfonamide and sodium o-benzoyl sulfimide, but the greatest effect is observed when zinc is in combination with the Class I compounds.
5. In reference to the concentrations studied, it is concluded that the effectiveness of zinc increases directly with increase in concentration in the Watts Bath.
6. Class I addition agents make up for a loss of effectiveness due to concentration, of the Class II compounds.
7. Zinc is more effective at the higher pH.
8. Sodium o-Benzoyl sulfimide is detrimental to the effect of benzene sulfonimide in the Watts Bath.
9. The addition agents have a smoothing effect regardless of whether the appearance of the plate is changed or not.
10. The subsurface must be considered before comparing the relative merits of addition agents as to their "smoothing power".

INTRODUCTION

PART II - Current Density-Cathode Efficiency Studies

Very few published data on cathode efficiencies are available. According to P. R. Pine[11], in connection with the efficiency of bright nickel plating baths, each system of addition agents operates within its own optimum limits as regards to pH, concentration, and temperature. Within each set of limits, there is a point at which maximum efficiency is attained, and this point usually lies in the neighborhood of 98% of theoretical. This maximum is not so much a function of pH of the solution as of the system of addition agents itself for various addition agents in the same bath at the same pH may give varied efficiencies. V. H. Waite[19], stated that sodium formate at a pH of 3.0 - 4.0 has a definite adverse effect on cathode efficiencies whereas amino polyaryl methanes have little effect and zinc and cadmium have a beneficial effect when added to normal amounts to nickel solutions containing aryl sulfonic acids. H. E. Haring[5], found that in a nickel sulfate solution, sodium citrate and sodium sulfite showed no improvement in cathode efficiencies, whereas hydrogen peroxide reduced cathode efficiency at low current densities. Somewhat later in 1925, P. A. Nickol[10] and O. P. Watts[10], found that nitrates lowered the cathode efficiency of nickel sulfate solutions by as much as 99%. The only recent publication the author could locate concerning cathode efficiencies of modern nickel baths was by W. A. Wesley and E. J. Roehl[21], in which they investigated four baths for the effect of current density on cathode current

efficiency. Their research, however, was not concerned with addition agents, and thus it was decided to investigate any effects the previously mentioned Class I and Class II addition agents might have on the cathode efficiencies of the High Chloride and Watts Type baths.

EXPERIMENTAL

All the data shown in Tables X-XX, and plotted in Fig. 38 - Fig. 42 inclusive, was obtained by use of a cell similar to W. A. Wesley and E. J. Roehl's[21] modified Haring cell. The cell, having inside dimensions, 60 cm. length, 10 cm. width and 13 cm. deep, was constructed of lucite sections 1 cm. thick. Slots were made at each end of the cell for holding the cathodes, and additional slots were made 40 cm. from each end and 10 cm. from one end for placing the anode at various positions in relation to the cathodes. Throughout these determinations only one cathode was used, however, and this was placed 40 cm. from the anode. The cathode was of sheet nickel with an outside coating or plate, deposited from the solution under examination. The anode consisted of nine parallel rods of electrolytic nickel, each approximately 0.3 cm. in diameter and 14 cm. in length, and silver soldered at intervals of 1 cm. to a nickel wire which rested on the edges of the cell when the anode was securily seated in position. The temperature of the solutions was maintained at 50.0 $\pm$ 1.0°C. by means of a constant temperature water bath. No mechanical means of agitation was employed as convection currents were deemed adequate to prevent polarization during a run. The solutions were purified and the addition agents added exactly as explained in the Experimental Procedure of Part I. A two liter copper coulometer[18] consisting of 1000 grams of water, 150 grams of cupric sulfate ($CuSO_4 \cdot 7H_2O$), 50 grams of concentrated sulfuric acid and 50 grams of ethyl alcohol was connected in series

with the lucite cell. The size of the copper cathode used depended upon the current density employed as it was deemed necessary to maintain the current density between 0.2 - 2.0 amps. per sq. dm. Since the range studied was 0.2 - 4.0 amps. per sq. dm. it was only necessary to use two different size cathodes having an effective area of 1 sq. dm. and 2 sq. dm. The pure sheet copper cathode was prepared for a run by dipping in 5% sulfuric acid for 10 seconds, rinsing in running water, distilled water, and a 10 - 90% (by volume) ether-ethyl alcohol mixture, and wiped dry with a clean cheese cloth. It was then weighed accurately on an analytical balance, given another 5 second sulfuric acid dip, distilled water rinse and placed in the coulometer. The sheet nickel cathode, at the beginning of the runs, was given an alkaline reverse electrocleaning, water rinse, 20% hydrochloric acid dip for ten seconds distilled water rinse, and plated with the first solution under test for thirty minutes at 3 amps. per sq. dm. The cathode was then removed from the cell, rinsed in distilled water, the ether-alcohol mixture, and wiped dry with a clean cheesecloth. It was then weighed, given another 5 second 20% hydrochloric acid dip, running and distilled water rinse, and placed immediately into the cell which had been previously regulated for proper current by means of dummy electrodes. The plating time, as determined by a stop watch, was for either twenty or thirty minutes. The same nickel cathode was used for all determinations, but was plated with the solution under test, as explained above, before any measurements were taken.

Furthermore, between the runs at the different current densities for any individual solution, the cathode was merely given a five second acid dip to remove the alcohol film, rinsed, and placed in the cell. The loss in weight incurred by the action of the acid dip was found to be insignificant.

TABLE X

Solution No. 8
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.209	.1241	.1098	95.81
.30	.314	.1863	.1667	96.90
.40	.423	.2511	.2253	97.20
.60	.610	.3615	.3289	98.50
1.00	1.013	.6411	.5859	98.93
2.50	2.516	1.4925	1.3682	99.25
4.00	4.146	2.4580	2.2590	99.49

TABLE XI

Solution No. 10
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.193	.1143	.1028	97.34
.30	.302	.1789	.1612	97.58
.40	.408	.2422	.2197	98.21
.80	.810	.4804	.4388	98.90
1.00	1.033	.6126	.5600	98.95
3.80	3.739	2.2172	2.0302	99.13

TABLE XII

Solution No. 13
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.191	.1134	.1009	96.37
.30	.307	.1820	.1641	97.62
.40	.398	.2440	.2203	97.74
.80	.799	.4893	.4431	98.03
1.00	1.082	.6418	.5810	98.10
4.2	4.217	2.5009	2.2851	98.92

TABLE XIII

Solution No. 15
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.202	.1198	.1075	97.10
.40	.402	.2382	.2160	98.18
.60	.585	.3470	.3168	98.84
.80	.808	.4790	.4378	98.94
1.00	.942	.5586	.5120	98.80
3.00	2.963	1.7570	1.6125	99.35

TABLE XIV

Solution No. 16
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.201	.1193	.1075	97.50
.30	.299	.1830	.1656	98.00
.40	.405	.2405	.2190	98.40
.80	.807	.4784	.4396	99.40
1.00	1.021	.6054	.5560	99.40
3.70	3.601	2.1352	1.9648	99.62

TABLE XV

Solution No. 19
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.198	.1177	.1039	95.58%
.30	.291	.1729	.1541	96.49
.40	.401	.2380	.2149	97.77
.80	.801	.4750	.4314	98.32
1.00	1.009	.5983	.5429	98.25
3.50	3.621	2.1473	1.9534	98.48

TABLE XVI

Solution No. 24
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 20-30 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.183	.0725	.0535	79.85
.30	.304	.1203	.0939	84.49
.40	.394	.2338	.1911	88.47
1.00	1.079	.4265	.3704	94.01
4.00	4.070	1.6895	1.5169	97.20

TABLE XVII

Solution No. 27
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 20 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.194	.0769	.0684	96.33
.30	.299	.1182	.1068	97.80
.40	.391	.1546	.1413	98.94
.80	.808	.3194	.2933	99.42
1.00	1.029	.4273	.3924	99.45
4.00	4.770	1.8850	1.7361	99.70

TABLE XVIII

Solution No. 29
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 20 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.194	.0768	.0677	95.5
.30	.301	.1190	.1072	97.5
.40	.407	.1479	.1338	97.8
.60	.606	.2400	.2179	98.3
1.00	1.05	.4155	.3802	99.25
3.50	3.45	1.3691	1.2540	99.30

TABLE XIX

Solution No. 34
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 20 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.190	.0752	.0665	95.70
.30	.308	.1281	.1135	96.10
.60	.609	.2411	.2181	98.00
.85	.858	.3391	.3112	99.40
1.0	1.045	.4138	.3810	99.45
3.0	3.177	1.2564	1.1541	99.48

TABLE XX

Solution No. 36
DATA AND RESULTS FOR CATHODE EFFICIENCIES
Temperature = 50°C., pH = 3.0 (electrometric), Time = 20 minutes

Amperes Observed	Amperes Calculated	Wt. of Copper Grams	Wt. of Nickel Grams	Percent Efficiency
.20	.194	.0768	.0693	97.70
.40	.407	.1477	.1359	99.40
.80	.803	.3173	.2919	99.59
1.00	1.114	.4405	.4064	99.88
4.0	4.320	1.7081	1.5758	99.87

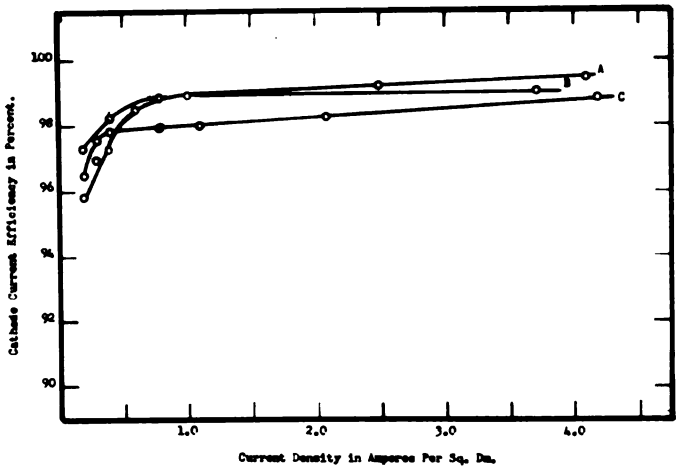

Fig.39. Cathode Current Efficiency-Current Density Curves. Temp. 50°C. pH-3.0

Curves: A. Solution 8; B. Solution 10; C. Solution 13.

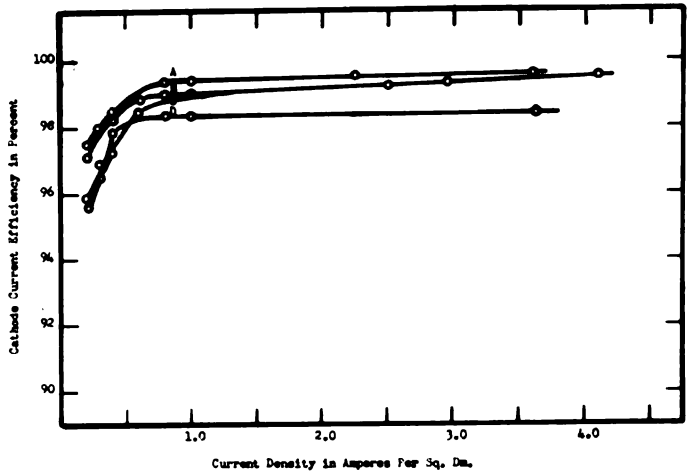

Fig.40.- Cathode Current Efficiency-Current Density Curves; Temp. 50°C. pH- 3.0

Curves: A. Solution 16; B. Solution 15; C. Solution 8; D. Solution 19.

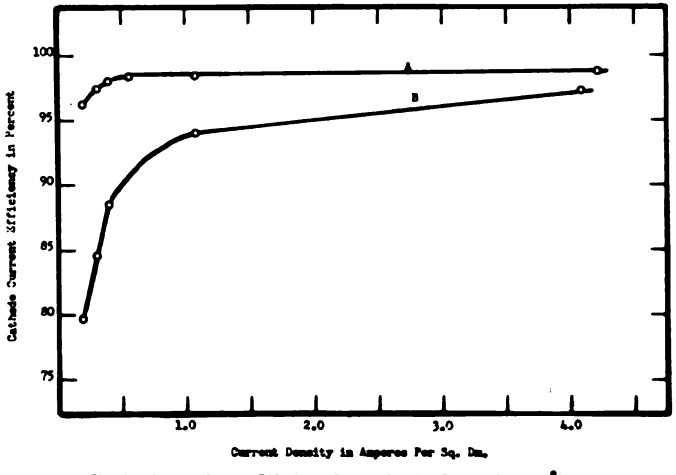

Fig.41.- Cathode Current Efficiency-Current Density Curves: Temp. 50°C. pH-3.0

Curves: A. Solution 13; B. Solution 24.

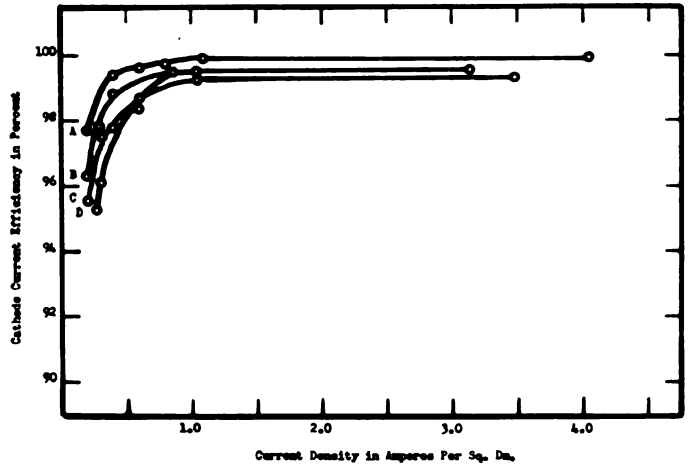

Fig.42.- Cathode Current Efficiency-Current Density Curves: Temp. 50°C. pH-3.0

Curves: A. Solution 36; B. Solution 27; C. Solution 29; D. Solution 34.

DISCUSSION OF RESULTS

PART II

The data and results obtained in this phase of the investigation are shown in Tables IX to XIX and graphed for further simplicity of comparison in Figures 39 - 42 inclusive. The results at current densities above 1 ampere per sq. dm. were reproducible to within approximately ± .5 percent, whereas at current densities below 1 ampere per sq. dm. where the slope of the curves are more vertical, the reproducibility was only within 2-3 percent.

All of the solutions investigated with the exception of solution 24 exhibited cathode current efficiencies within a range extending from 95% at low current densities to 99.9% at high current densities. The efficiencies of solution 24, containing sodium o-benzoyl sulfimide, benzene sulfonamide, 16 g./l. of PQ, sodium lauryl sulfate and sodium fluoborate, however, varied from approximately 80% to 97% as is shown in Curve B, Figure 41. Solution 13, Curve A, Figure 41, contains the same constituents as solution 24 with the exception of the PQ and sodium fluoborate and its efficiency is 16% higher at the lowest current density. This difference is minimized, however, with an increase in current density until at 4 amperes per sq. dm., the difference is only 1.5 percent. Thus it is readily concluded that nickel solutions containing PQ and its non-pitter counterpart sodium fluoborate should be operated at current densities in the vicinity of 4 amperes per sq. dm. for maximum efficiency.

Figures 39 and 42 indicate a slight beneficial effect when .9 g./l. zinc sulfate ($ZnSO_4.7H_2O$) is added to either the Watts or High Chloride baths, but this is only approximately 1% which is not particularly significant. .5 g./l. zinc sulfate ($ZnSO_4.7H_2O$), however, shows no effect above 1 ampere per sq. dm. and very little beneficial effect below, which indicates the importance of concentration of zinc in nickel baths.

In Figure 39, solution 10 containing benzene sulfonamide and solution 13 containing benzene sulfonamide plus sodium o-benzoyl sulfimide appear to be somewhat beneficial at current densities below 1 ampere per sq. dm. and slightly detrimental above 1 ampere per sq. dm., the latter solution lowering the efficiencies slightly more than the former. This indicates that sodium o-benzoyl sulfimide has a slight harmful effect on cathode efficiencies. No conclusions can be advanced as to whether the two above mentioned addition agents actually increase cathode efficiency at low current densities or not because the slight improvement is well within the experimental error. Figure 42, curve C, shows the same tendency for sodium o-benzoyl sulfimide in the High Chloride bath.

The curve for solution 19, Figure 40, is rather interesting as it indicates that a solution containing both zinc and benzene sulfonamide lowers the efficiency of not only the standard bath, Solution 8, but also the solutions containing either zinc (Solution 16) or benzene sulfonamide (Solution 10) individually. This would suggest that either is somewhat detrimental to the other but the

benzene sulfonamide has a more harmful effect on the zinc than visa versa.

In the High Chloride bath, as evidenced in Figure 42, Solution 34, containing both addition agents of Class I plus zinc, has a lower efficiency than solution 36, which contains only zinc as an addition agent. Here again the Class I addition agents have a harmful effect on the beneficial properties of zinc.

CONCLUSIONS

The important conclusions gleaned from the results of Part II are:

1. PQ is the only addition agent investigated that shows significant harmful effects on the cathode efficiencies, especially at current densities below 3-4 amperes per sq. dm.
2. For maximum efficiency of solutions containing PQ, the current density should be at least 4 amperes per sq. dm.
3. Zinc, sodium o-benzoyl sulfimide, and benzene sulfonamide individually or in combination have little beneficial or harmful effect on either the Watts or High Chloride baths.
4. Zinc definitely effects a slight increase in efficiency at the higher concentrations.
5. The Class I compounds show a slight detrimental effect by themselves and also decrease the efficiency of the solutions containing zinc.

INTRODUCTION

PART III - Current Density - Potential Measurements

The author found few publications dealing with the effect of addition agents, in nickel plating baths, upon current density - potential relationships. J. Haas[4], added benzoic, tartaric, acetic, and succinic acids to nickel baths and found they displaced the cathode - potential curve too far to the negative side to be of value as addition agents. Haring[5], found that sodium citrate and dextrin increased the cathodic curve negatively in nickel solutions. He also found that an all chloride bath caused a more negative cathodic potential curve than did a pure nickel sulfate bath. C. T. Thomas and W. Blum[17], studied the anode potential - current density curves for various nickel anodes in nickel solutions. They found that abnormally high anode potentials were present in nickel solutions free of chlorides. This is attributed to anode passivity. The same authors also mentioned the fact that a high anode potential is directly related to the resistance of the bath. A few tenths of a volt difference in potential for any given current density is insignificant, but a difference of over one volt may cause the power loss due to passivity to become appreciable. Dorrance and Gardiner[3], also noted that the chloride ion causes a large shift of the anode current density - potential curves to a less positive value, thus indicating the corrosive ability of this ion. E. Raub and M. Wittum[14], found in studying nitrogen compound addition agents that formamide, urea, and urethane increase the cathode potential curve negatively.

Sulfur compounds such as thiourea also displaced the curve toward the negative side. Protein addition agents such as dextrose and sucrose displace the curve to the more positive side. The weak brighteners of the aliphatic class appear to have little effect on the curves, while the strong brighteners cause an increase in the cathode curves toward the negative side. W. A. Wesley and E. J. Roehl[21], also made some cathode potential - current density measurements using four modern nickel baths, but their investigation was not concerned with addition agents.

Since comparatively little research has been conducted in regards to the effect of modern addition agents in potential curves, it was decided in this phase of the investigation to obtain anode, cell, and cathode potential data for several of the solutions in Table II. The current density-potential curves thus obtained can be used by themselves or in conjunction with other information to explain many phenomena of nickel deposition such as throwing power, anode corrosion, and structure of the deposit. These problems, however, are beyond the scope of this investigation for it is merely the intention of the author to secure useful curves that will indicate the effect, if any, of addition agents on potential measurements.

EXPERIMENTAL

All measurements of cell, anode, and cathode potentials were made in a four compartment pyrex cell, each compartment being 5 inches deep, and $1\frac{1}{2}$ inches in internal diameter. The first and second, and the third and fourth compartments were connected by ground-glass stopcocks, whereas the second and third compartments were fastened together through a glass connection $\frac{1}{2}$ inch in internal diameter. The cathode was of sheet steel coated with nickel deposited from the solution under test and having an effective area of 1/120 sq. ft. The anode was electrolytic nickel having an area of 1/130 sq. ft. The electrolytic temperature was maintained throughout most of the work at 50°C. by means of a constant - temperature water bath. Some determinations were also carried out at 25°C. and 75°C., for the purpose of comparison. A Leeds and Northrup Potentiometer, and a model 280, Weston, d.c. ammeter, each scale division reading .002 amperes, were used to measure voltage and amperage respectively. The anode and cathode potentials were measured by means of separate 1 n.calomel cells placed in the first and fourth compartments. The composition of the solutions used are shown in Table II, and were prepared exactly as explained in Part I.

During a run, the solution was placed in the cell to a depth of four inches or just above the stopcock connections. The ground glass stopcocks permitted the passage of current but at the same

time prevented any diffusion of electrolytes. The cell was then placed in the water bath and allowed to reach thermal equilibrium at 50°C. The calomel cells were then placed in compartments one and four. The anode and cathode were then placed in the center of compartments 2 and 3 respectively, directly opposite the central glass connection, and fastened securely $2\frac{1}{4}$ inches apart by pure nickel wire suspended through rubber stoppers. The electrodes and calomel cells were then connected by means of copper wire through a threeway switch to the potentiometer. An external circuit containing a 6 volt storage battery, a 3,360 ohm slide resistor and the ammeter was connected in series with the cell under test. By means of the slide wire resistor, the current was gradually increased in the external circuit, and by a manipulation of the switch, the anode, cell, and cathode potentials were obtained directly for each current density. The current was permitted to reach equilibrium, which it usually did, in one or two minutes, before taking any potential readings. Since relative effects only were to be determined, and since the resistance of any one bath would be constant, it was deemed neither necessary nor important to measure the IR drop of the solution. Throughout these measurements the calomel cells were connected to the positive and the two electrodes to the negative poles of the potentiometer when anode and cathode potentials were desired. In Tables XI - LXVII, the potential values are shown in reference to both the calomel and hydrogen electrodes. The latter values were calculated by subtracting all measured potentials

from +.2800. Either values would be perfectly acceptable to use for comparison of results, but the hydrogen scale data was used in the plotting of all anode and cathode potential curves.

All potential measurements recorded in the following tables (XXI-LVIII) are expressed in volts. The anode and cathode potential measurements as obtained by means of the 1n. calomel cells are converted to the hydrogen cell scale by subtracting all values from -.2800. The cathode area equals 1/120 sq. ft. and the anode area = 1/130 sq. ft.

TABLE XXI

CELL, ANODE, AND CATHODE POTENTIAL DATA

Temperature - 25°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3440	-.2750	.5555	+.0130	.2670
.0005	.3680	-.2950	.5750	+.0150	.2650
.001	.4032	-.3300	.6100	+.0315	.2485
.002	.4650	-.3600	.6400	+.0465	.2335
.003	.5180	-.3750	.6550	+.0649	.2151
.004	.5660	-.4070	.6870	+.0800	.2000
.005	.6155	-.4165	.6965	+.0930	.1870
.006	.6535	-.4230	.7030	+.1058	.1742
.008	.7145	-.4350	.7150	+.1188	.1612
.01	.7750	-.4460	.7260	+.1270	.1530
.016	.9290	-.4625	.7425	+.1395	.1405
.02	1.1300	-.4740	.7540	+.1510	.1290
.03	1.2760	-.5018	.7818	+.1570	.1230

TABLE XXII

Solution No. 1

CELL, ANODE, AND CATHODE POTENTIAL DATA

Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1765	-.2880	.5680	-.1200	.4000
.0005	.1925	-.2890	.5690	-.1075	.3875
.001	.2095	-.2890	.5690	-.1000	.3800
.002	.2445	-.2940	.5740	-.0820	.3620
.004	.3060	-.3025	.5825	-.0550	.3350
.006	.3470	-.3090	.5890	-.0505	.3305
.008	.3885	-.3180	.5980	-.0385	.3185
.01	.4335	-.3250	.6050	-.0300	.3100
.02	.6255	-.3495	.6295	+.0095	.2705
.04	.9575	-.3785	.6585	+.0515	.2285
.06	1.2700	-.3970	.6770	+.0755	.2045

TABLE XXIII

Solution No. 1

CELL, ANODE, AND CATHODE POTENTIAL DATA

Temperature = 75°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1155	-.2530	.5330	-.1440	.4240
.0005	.1185	-.2540	.5340	-.1425	.4225
.001	.1305	-.2545	.5345	-.1350	.4150
.002	.1530	-.2575	.5375	-.1270	.4070
.004	.1920	-.2625	.5425	-.1130	.3930
.006	.2220	-.2650	.5450	-.1070	.3870
.008	.2490	-.2675	.5475	-.1000	.3800
.01	.2740	-.2715	.5515	-.0980	.3780
.016	.3470	-.2765	.5565	-.0840	.3640
.02	.3940	-.2815	.5615	-.0830	.3630
.03	.5020	-.2860	.5660	-.0685	.3485
.04	.6050	-.2920	.5720	-.0650	.3450
.06	.8440	-.3015	.5815	-.0450	.3250
.08	1.065	-.3090	.5890	-.0365	.3165

TABLE XXIV

Solution No. 2
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2145	-.3005	.5805	-.0890	.3690
.001	.2600	-.3165	.5965	-.0805	.3605
.002	.3145	-.3340	.6140	-.0610	.3410
.004	.3988	-.3625	.6425	-.0480	.3280
.006	.4505	-.3690	.6490	-.0300	.3100
.008	.4835	-.3725	.6535	-.0265	.3065
.01	.5220			-.0190	.2990
.016	.6415	-.3810	.6610	-.0100	.2900
.02	.7220	-.3850	.6650	-.0000	.2800
.03	.9155	-.3810	.6590	+.0200	.2600
.04	1.0910	-.3800	.6600	+.0360	.2440

TABLE XXV

Solution No. 3
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1750	-.2850	.5650	-.1220	.4020
.0005	.1900	-.2880	.5680	-.1090	.3890
.001	.2075	-.2900	.5700	-.1000	.3800
.002	.2410	-.2920	.5720	-.0825	.3625
.004	.3025	-.3000	.5800	-.0520	.3320
.006	.3450	-.3070	.5870	-.0500	.3300
.008	.3865	-.3150	.5950	-.0390	.3190
.01	.4325	-.3245	.6045	-.0310	.3110
.02	.6240	-.3500	.6300	+.0080	.2720
.04	.9550	-.3795	.6595	+.0510	.2290
.06	1.2690	-.3950	.6750	+.0735	.2065

TABLE XXVI

Solution No. 4
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1572	-.2610	.5410	-.1155	.3955
.001	.2115	-.2830	.5630	-.1020	.3820
.002	.2635	-.3120	.5920	-.0815	.3615
.004	.3430	-.3240	.6040	-.0580	.3380
.006	.4155	-.3505	.6305	-.0372	.3172
.008	.4700	-.3610	.6410	-.0255	.3055
.01	.5210	-.3660	.6460	-.0130	.2930
.016	.6625	-.3825	.6625	+.0130	.2670
.02	.7445	-.3880	.6680	+.0240	.2560
.03	.9355	-.3990	.6790	+.0445	.2365
.04	1.1250	-.4085	.6885	+.0545	.2255

TABLE XXVII

Solution No. 5
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 25°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.4695	-.3635	.6435	+.0935	.1865
.0005	.5575	-.3915	.6715	+.1250	.1550
.001	.6300	-.4300	.7100	+.1395	.1405
.002	.7220	-.4570	.7370	+.1610	.1190
.004	.8815	-.5000	.7800	+.1800	.1000
.006	1.0120	-.5190	.7990	+.2015	.0785

TABLE XXVIII

Solution No. 5
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2310	-.3186	.5986	-.0960	.3760
.0005	.2890	-.3385	.6185	-.0755	.3555
.001	.3750	-.3595	.6395	-.0320	.3120
.002	.4730	-.3850	.6650	+.0180	.2620
.004	.6160	-.4185	.6985	+.0560	.2240
.006	.7210	-.4360	.7160	+.0930	.1870
.008	.8009	-.4425	.7225	+.1050	.1750
.01	.8990	-.4530	.7330	+.1648	.1152
.02	1.2810	-.4750	.7550	+.1700	.1100

TABLE XXIX

Solution No. 5
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 75°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1995	-.3115	.5915	-.1235	.4035
.0005	.2250	-.3243	.6043	-.1195	.3995
.001	.2580	-.3345	.6145	-.1065	.3865
.002	.3550	-.3550	.6350	-.0480	.3280
.004	.4500	-.3650	.6450	-.0205	.3005
.006	.5250	-.3725	.6525	+.0045	.2755
.008	.6005	-.3785	.6585	+.0260	.2540
.01	.6860	-.3890	.6690	+.0510	.2290
.02	----	-.4250	.7050	+.1100	

TABLE XXX

Solution No. 6
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.4265	-.2875	.5675	+.1165	.1635
.001	.5112	-.3105	.5905	+.1455	.1345
.002	.5845	-.3345	.6145	+.1645	.1155
.004	.7200	-.3635	.6435	+.1795	.1005
.006	.8300	-.3980	.6780	+.1875	.0925
.008	.9360	-.4185	.6985	+.1975	.0825
.01	1.0350	-.4395	.7195	+.1985	.0815
.016	1.3055	-.4640	.7440	+.2118	.0682
.02	1.4680	-.4775	.7575	+.2145	.0655

TABLE XXXI

Solution No. 7
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 25°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3335	-.3200	.6000	+.0140	.2660
.0005	.4450	-.3650	.6450	+.0440	.2360
.001	.5365	-.4000	.6800	+.0650	.2150
.002	.6300	-.4110	.6910	+.0840	.1960
.003	.7085	-.4170	.6970	+.1080	.1720
.004	.7730	-.4410	.7210	+.1125	.1675
.006	.8940	-.4600	.7400	+.1195	.1605
.008	.9940	-.4750	.7550	+.1290	.1510
.01	1.1090	-.4850	.7650	+.1383	.1417
.016	----	-.5100	.7900	----	----
.02	----	-.5200	.8000	----	----
.03	----	-.5450	.8250	----	----

TABLE XXXII

Solution No. 7
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2650	-.3160	.5960	-.0565	.3365
.0005	.3240	-.3258	.6058	-.0325	.3125
.001	.4040	-.3805	.6605	-.0160	.2960
.002	.4655	----	----	+.0035	.2765
.003	.5100	-.3835	.6635	+.0195	.2605
.004	.5615	-.3966	.6760	+.0270	.2530
.006	.6495	-.4100	.6900	+.0450	.2350
.008	.7260	-.4208	.7008	+.0465	.2335
.01	.8090	-.4270	.7070	+.0560	.2240
.016	1.0160	-.4430	.7230	+.0670	.2130
.02	1.1380	-.4455	.7255	+.0750	.2050
.03	1.4240	-.4460	.7360	+.0718	.2082

TABLE XXXIII

Solution No. 7
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 75°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2130	-.3030	.5830	-.0950	.3750
.0005	.2515	-.3180	.5980	-.0860	.3660
.001	.2785	-.3230	.6030	-.0750	.3550
.002	.3210	-.3350	.6150	-.0675	.3475
.003	.3490	-.3300	.6100	-.0550	.3350
.004	.3795	-.3345	.6145	-.0540	.3340
.006	.4455	-.3450	.6250	-.0440	.3240
.008	.5065	-.3545	.6345	-.0415	.3215
.01	.5725	-.3650	.6450	-.0310	.3110
.016	.7440	-.3820	.6620	-.0220	.3020
.02	.8630	-.3970	.6770	-.0160	.2960
.03	1.1270	-.4075	.6875	-.0065	.2865
.04	1.3870	-.4200	.7000	+.0090	.2710

TABLE XXXIV

Solution No. 9
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50o C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3825	-.3315	.6115	+.0335	.2465
.001	.4455	-.3530	.6330	+.0570	.2230
.002	.5110	-.3740	.6540	+.0610	.2190
.004	.6270	-.4025	.6825	+.0800	.2000
.006	.6172	-.4200	.7000	+.0870	.1930
.008	.7940	-.4350	.7150	+.0965	.1835
.01	.8765	-.4510	.7310	+.1000	.1800
.016	1.0775	-.4590	.7390	+.1105	.1695
.02	1.1975	-.4645	.7445	+.1130	.1670
.03	1.5150	-.4690	.7490	+.1190	.1610

TABLE XXXV

Solution No. 9
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 75°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2505	-.2680	.5480	-.0585	.3385
.001	.2935	-.3025	.5825	-.0460	.3260
.002	.3470	-.3155	.5955	-.0308	.3108
.004	.4370	-.3355	.6155	-.0200	.3000
.006	.5080	-.3518	.6318	-.0090	.2890
.008	.5860	-.3710	.6510	-.0035	.2835
.01	.6525	-.3885	.6685	+.0070	.2730
.016	.8455	-.4085	.6885	+.0215	.2585
.02	.9460	-.4110	.6910	+.0315	.2485
.03	1.2180	-.4115	.6915	+.0465	.2335

TABLE XXXVI

Solution No. 11
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2465	-.2700	.5500	-.0510	.3310
.001	.3265	-.2912	.5712	-.0250	.3050
.002	.4220	-.3230	.6030	-.0040	.2840
.004	.5600	-.3325	.6325	+.0180	.2620
.006	.6792	-.3630	.6630	+.0385	.2415
.008	.7830	-.3825	.6825	+.0400	.2400
.01	.8718	-.3822	.6822	+.0495	.2305
.016	1.1275	-.4020	.7020	+.0570	.2230
.02	1.2880	-.4120	.7120	+.0630	.2170
.026	1.4980	-.4160	.7160	+.0708	.2092

TABLE XXXVII

Solution No. 12
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3000	-.2815	.5615	-.0200	.3000
.001	.4060	-.3330	.6130	+.0225	.2575
.002	.4775	-.3565	.6365	+.0435	.2365
.004	.6020	-.3850	.6650	+.0675	.2125
.006	.7060	-.4200	.7000	+.0700	.2100
.008	.7825	-.4330	.7130	+.0815	.1985
.01	.8615	-.4330	.7130	+.0885	.1915
.02	1.2310	-.4650	.7450	+.1200	.1600
.03	1.5600	-.4805	.7605	+.1280	.1520

TABLE XXXVIII

Solution No. 12
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 75°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2180	-.2775	.5575	-.0710	.3510
.001	.2880	-.3125	.5925	-.0470	.3270
.002	.3380	-.3200	.6000	-.0440	.3240
.004	.4165	-.3440	.6240	-.0280	.3080
.006	.5050	-.3595	.6395	-.0260	.3060
.008	.5750	-.3775	.6575	-.0125	.2925
.01	.6430	-.3890	.6690	-.0085	.2885
.02	.9385	-.4060	.6860	+.0185	.2615

TABLE XXXIX

Solution No. 14
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3025	-.3070	.5870	-.0180	.2980
.001	.4165	-.3665	.6465	-.0065	.2865
.002	.4890	-.3990	.6790	+.0183	.2617
.004	.5865	-.4235	.7035	+.0255	.2545
.006	.6550	-.4265	.7065	+.0345	.2455
.008	.7410	-.4350	.7150	+.0400	.2400
.01	.8030	-.4400	.7200	+.0440	.2360
.016	1.0180	-.4440	.7240	+.0605	.2195
.02	1.1410	-.4495	.7295	+.0625	.2175
.03	1.4510	-.4510	.7310	+.0785	.2015

TABLE XL

Solution 15
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2410	-.2690	.5490	-.0475	.3275
.001	.3550	-.3415	.6215	-.0227	.3027
.002	.4400	-.3720	.6520	-.0055	.2855
.004	.5500	-.3980	.6780	+.0150	.2650
.006	.6382	-.4160	.6960	+.0255	.2545
.008	.7180	-.4250	.7050	+.0380	.2420
.01	.7930	-.4325	.7125	+.0340	.2460
.016	1.0080	-.4495	.7295	+.0605	.2195
.02	1.1330	-.4550	.7350	+.0605	.2195
.03	1.4695	-.4670	.7470	+.0760	.2040

TABLE XLI

Solution No. 16
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50°C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2290	-.2568	.5368	-.0425	.3225
.001	.3130	-.3135	.5935	-.0240	.3040
.002	.4235	-.3630	.6430	-.0110	.2910
.004	.5420	-.3930	.6730	+.0120	.2680
.006	.6310	-.4165	.6965	+.0210	.2590
.008	.7112	-.4265	.7065	+.0335	.2465
.01	.7930	-.4365	.7165	+.0390	.2410
.016	1.0020	-.4500	.7300	+.0565	.2235
.02	1.1265	-.4615	.7415	+.0560	.2240
.03	1.4435	-.4650	.7450	+.0705	.2095

TABLE XLII

Solution No. 17
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2860	-.3130	.5930	-.0500	.3300
.001	.3425	-.3250	.6050	-.0260	.3060
.002	.4135	-.3510	.6310	-.0145	.2945
.004	.5225	-.3755	.6555	+.0110	.2690
.006	.5930	-.3925	.6725	+.0180	.2620
.008	.6625	-.3925	.6725	+.0265	.2535
.01	.7280	-.3995	.6795	+.0295	.2505
.016	.9340	-.4045	.6845	+.0475	.2325
.02	1.0600	-.4150	.6950	+.0570	.2230
.03	1.3830	-.4225	.7025	+.0740	.2060

TABLE XLIII

Solution No. 18
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3210	-.3315	.6115	-.0300	.3100
.001	.3825	-.3560	.6360	-.0075	.2875
.002	.4445	-.3705	.6505	+.0055	.2745
.004	.5312	-.3810	.6610	+.0225	.2575
.006	.6100	-.3945	.6745	+.0275	.2525
.008	.6880	-.4030	.6830	+.0375	.2425
.01	.7455	-.4092	.6892	+.0390	.2410
.016	.9635	-.4210	.7010	+.0575	.2225
.02	1.0920	-.4285	.7085	+.0575	.2225
.03	1.4215	-.4450	.7250	+.0780	.2020

TABLE XLIV

Solution No. 19
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2745	-.3115	.5915	-.0510	.3310
.001	.3540	-.3465	.6265	-.0300	.3100
.002	.4315	-.3738	.6538	-.0105	.2905
.004	.5195	-.3810	.6610	+.0088	.2712
.006	.6015	-.3930	.6730	+.0190	.2610
.008	.6830	-.4050	.6850	+.0265	.2535
.01	.7565	-.4090	.6890	+.0380	.2420
.016	.9765	-.4280	.7080	+.0510	.2290
.02	1.1120	-.4325	.7125	+.0625	.2175
.03	1.4515	-.4530	.7330	+.0780	.2020

TABLE XLV

Solution No. 20
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2170	-.2355	.5155	-.0332	.3132
.0006	.2942	-.2655	.5455	-.0125	.2925
.0016	.4070	-.3390	.6190	+.0090	.2710
.0028	.5692	-.4022	.6822	+.0285	.2515
.0054	.7175	-.4460	.7260	+.0525	.2275
.0078	.8226	-.4590	.7390	+.0605	.2195
.0090	.8850	-.4600	.7400	+.0685	.2115
.0130	1.0640	-.4785	.7585	+.0770	.2030
.0190	1.3165	-.4875	.7675	+.0930	.1870
.0246	1.5585	-.4950	.7750	+.1055	.1745

TABLE XLVI

Solution No. 23
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3250	-.3055	.5855	+.0050	.2750
.0006	.3625	-.3155	.5955	+.0290	.2610
.001	.4082	-.3345	.6145	+.0330	.2470
.002	.4965	-.3572	.6372	+.0445	.2355
.0038	.6065	-.3990	.6790	+.0635	.2165
.0059	.7400	-.4266	.7066	+.0784	.2016
.0078	.8360	-.4568	.7368	+.0850	.1950
.0095	.9318	-.4710	.7510	+.0874	.1926
.0121	1.0690	-.4920	.7720	+.1010	.1790
.0160	1.2430	-.5110	.7910	+.1115	.1685
.0235	1.5466	-.5190	.7990	+.1295	.1505
.0298	----	-.5240	.8040	+.1370	.1430
.0373	----	-.5310	.8110	+.1445	.1355

TABLE XLVII

Solution No. 26
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 25° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3130	-.2950	.5750	+.0650	.2150
.0005	.3885	-.3405	.6205	+.0680	.2120
.001	.4340	-.3615	.6415	+.0770	.2030
.002	.5090	-.3888	.6688	+.0870	.1930
.003	.5695	-.4025	.6825	+.1005	.1795
.004	.6095	-.4130	.6930	+.1060	.1740
.006	.6875	-.4250	.7050	+.1170	.1630
.008	.7545	-.4360	.7160	+.1195	.1605
.01	.8195	-.4410	.7210	+.1235	.1565
.016	.9935	-.4565	.7365	+.1310	.1490
.02	1.1085	-.4620	.7420	+.1375	.1425
.03	1.3755	-.4750	.7550	+.1445	.1365

TABLE XLVIII

Solution No. 26
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2160	-.3150	.5950	-.0995	.3795
.0005	.2670	-.3390	.6190	-.0865	.3665
.001	.2965	-.3450	.6250	-.0700	.3500
.002	.3330	-.3600	.6400	-.0580	.3380
.004	.3720	-.3615	.6415	-.0425	.3225
.006	.4040	-.3695	.6495	-.0405	.3205
.008	.4625	-.3825	.6625	-.0230	.3030
.01	.5230	-.3745	.6545	-.0230	.3030
.016	.6500	-.3890	.6690	-.0050	.2850
.02	.7275	-.3905	.6705	+.0065	.2735
.03	.9035	-.3950	.6750	+.0175	.2625
.04	1.0880	-.4080	.6880	+.0360	.2440

TABLE XLIX

Solution No. 26
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 75° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.0970	-.2480	.5280	-.1540	.4340
.0005	.1205	-.2570	.5320	-.1485	.4285
.001	.1435	-.2675	.5475	-.1390	.4190
.002	.1750	-.2770	.5570	-.1315	.4115
.003	.1950	-.2770	.5570	-.1225	.4025
.004	.2120	-.2795	.5595	-.1225	.4025
.006	.2580	-.2895	.5695	-.1107	.3907
.008	.2995	-.2975	.5775	----	----
.01	.3370	-.3060	.5860	-.1020	.3820
.016	.4385	-.3200	.6000	-.0905	.3705
.02	.5010	-.3260	.6060	-.0855	.3655
.03	.6495	-.3405	.6205	-.0750	.3550
.04	.7910	-.3520	.6320	-.0710	.3510
.06	1.099	-.3675	.6475	-.0505	.3305

TABLE L

Solution No. 28
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2390	-.3232	.6032	-.0920	.3720
.001	.2835	-.3290	.6090	-.0700	.3500
.002	.3285	-.3345	.6145	-.0525	.3325
.004	.4200	-.3550	.6350	-.0315	.3115
.006	.4855	-.3680	.6480	-.0145	.2945
.008	.5450	-.3815	.6615	-.0110	.2910
.01	.5960	-.3850	.6650	-.0040	.2840
.016	.7575	-.4060	.6860	+.0120	.2680
.02	.8575	-.4120	.6920	+.0260	.2540
.03	1.1000	-.4265	.7065	+.0435	.2365
.04	1.3320	-.4320	.7120	+.0570	.2230

TABLE LI

Solution No. 30
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 25° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3090	-.2995	.5795	+.0065	.2735
.001	.4295	-.3525	.6325	+.0286	.2514
.002	.5175	-.3950	.6750	+.0635	.2165
.004	.6125	-.4200	.7000	+.0900	.1900
.006	.6800	-.4200	.7000	+.1075	.1725
.008	.7400	-.4180	.6980	+.1165	.1635
.01	.8130	-.4350	.7150	+.1238	.1562
.016	1.0010	-.4475	.7275	+.1415	.1385
.02	1.1210	-.4570	.7370	+.1425	.1375
.04	1.3960	-.4775	.7575	+.1565	.1235

TABLE LII

Solution No. 30
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1790	-.2635	.5435	-.1000	.3800
.001	.2405	-.3009	.5809	-.0800	.3600
.002	.2730	-.3090	.5890	-.0720	.3520
.004	.3460	-.3240	.6040	-.0500	.3300
.006	.4050	-.3380	.6180	-.0425	.3225
.008	.4530	-.3465	.6265	-.0345	.3145
.01	.5050	-.3530	.6330	-.0275	.3075
.016	.6425	-.3665	.6465	-.0075	.2875
.02	.7330	-.3780	.6580	+.0010	.2790
.04	1.1475	-.4005	.6805	+.0525	.2275

TABLE LIII

Solution No. 31
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 25° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.3275	-.3335	.6135	.0000	.2800
.0005	.3890	-.3615	.6415	+.0190	.2610
.001	.4230	-.3860	.6660	+.0300	.2500
.002	.5365	-.4340	.7140	+.0940	.1860
.004	.6720	-.5245	.8045	+.1530	.1270
.005	.7240	-.5500	.8300	+.1765	.1035
.006	.7575	-.5630	.8430	+.1920	.0880
.008	.8210	-.5995	.8795	+.2275	.0525
.01	.8790	-.6175	.8975	+.2615	.0185
.016	1.0580	-.7090	.9890	----	----

TABLE LIV

Solution No. 31
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0005	.2090	-.2990	.5790	-.1015	.3815
.001	.2648	-.3185	.5785	-.0795	.3595
.002	.3042	-.3315	.6115	-.0660	.3460
.004	.3800	-.3490	.6290	-.0475	.3275
.005	.4158	-.3635	.6435	-.0390	.3190
.006	.4430	-.3725	.6525	-.0385	.3185
.008	.4955	-.3820	.6620	-.0270	.3070
.01	.5425	-.3880	.6680	-.0255	.3055
.016	.6795	-.3995	.6795	-.0030	.2830
.02	.7580	-.4050	.6850	+.0010	.2790
.03	.9580	-.4115	.6915	+.0300	.2500
.04	1.1485	-.4220	.7020	+.0375	.2425
.06	1.5120	-.4310	.7110	+.0615	.2185

TABLE LV

Solution No. 32
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2340	-.3165	.5965	-.0880	.3680
.001	.2735	-.3240	.6040	-.0785	.3585
.002	.3150	-.3255	.6055	-.0580	.3380
.004	.3895	-.3380	.6180	-.0425	.3225
.006	.4560	-.3450	.6250	-.0300	.3100
.008	.5160	-.3585	.6385	-.0242	.3042
.01	.5960	-.3690	.6490	-.0145	.2945
.016	.7675	-.3885	.6685	+.0080	.2720
.02	.8755	-.4005	.6805	+.0175	.2625
.03	1.1440	-.4155	.6955	+.0395	.2405
.04	1.3950	-.4260	.7060	+.0585	.2215

TABLE LVI

Solution No. 33
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.2285	-.3050	.5850	-.0845	.3645
.001	.2825	-.3195	.5995	-.0655	.3455
.002	.3425	-.3390	.6190	-.0500	.3300
.004	.4255	-.3600	.6400	-.0330	.3130
.006	.4985	-.3750	.6550	-.0210	.3010
.008	.5520	-.3825	.6625	-.0130	.2930
.01	.6115	-.3875	.6675	-.0055	.2855
.016	.7742	-.4020	.6820	+.0135	.2665
.02	.8800	-.4080	.6880	+.0245	.2555
.03	1.1340	-.4205	.7005	+.0380	.2420
.04	1.3800	-.4290	.7090	+.0470	.2230

TABLE LVII

Solution No. 34
CELL, ANODE, AND CATHODE POTENTIAL DATA
Temperature = 50° C. pH = 3.0 (electrometric)

Amperes	Cell Potential	Cathode-Potential		Anode-Potential	
		Hydrogen	Calomel	Hydrogen	Calomel
.0001	.1810	-.2580	.5380	-.0905	
.001	.2302	-.2740	.5540	-.0795	
.002	.3540	-.3755	.6555	-.0660	
.004	.4820	-.4300	.7100	-.0500	
.006	.5420	-.4345	.7145	-.0400	
.008	.5972	-.4405	.7205	-.0300	
.01	.6415	-.4405	.7205	-.0260	
.016	.8290	-.4665	.7465	-.0050	
.02	.9430	-.4810	.7610	+.0088	
.03	1.2002	-.5062	.7862	+.0280	
.04	1.4295	-.4865	.7665	+.0480	

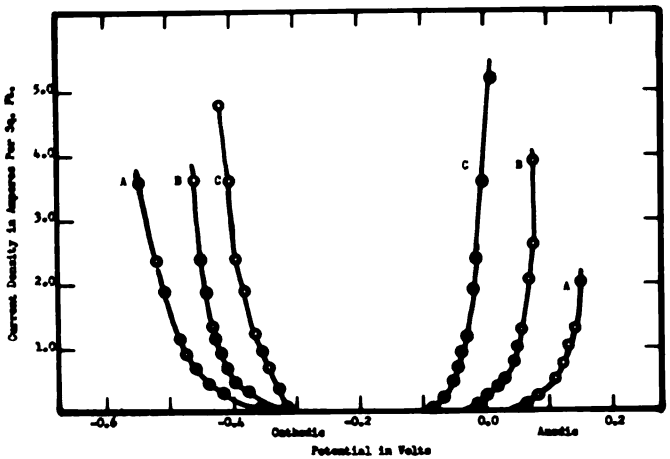

Fig.43. Current Density-Potential Curves(Hydrogen Cell Scale)

Curves: A. Solution 7 at 25°C; B. Solution 7 at 50°C; C. Solution 7 at 75°C.

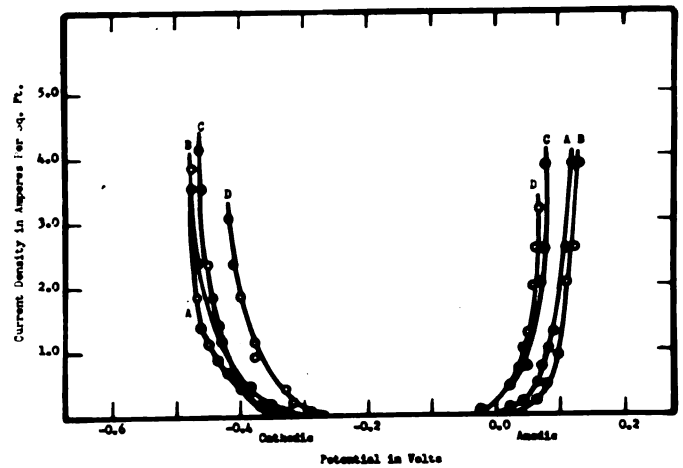

Fig.44. Current Density-Potential Curves at 50°C(Hydrogen Cell Scale)

Curves: A. Solution 12; B. Solution 9; C. Solution 7; D. Solution 11.

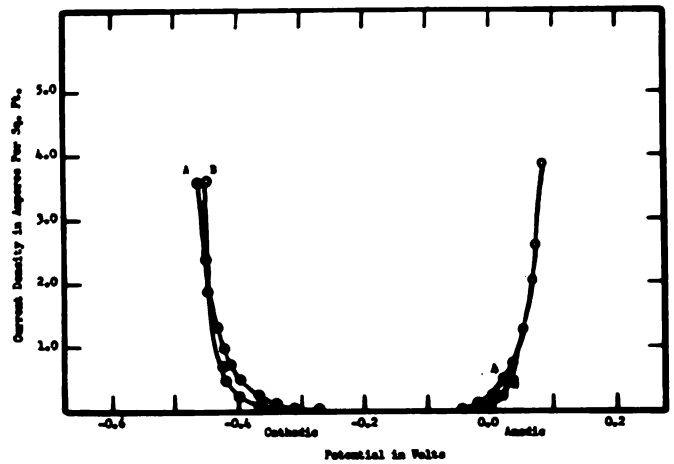

Fig.45. Current Density-Potential Curves at 50°C.(Hydrogen Cell Scale)

Curves: A. Solutions 7,15,and; B. Solution 14.

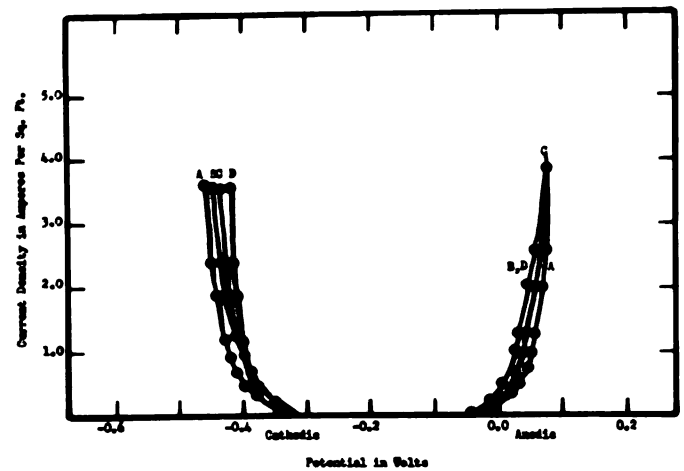

Fig.46. Current Density-Potential Curves at 50°C.(Hydrogen Cell Scale)

Curves: A. Solution 7; B. Solution 19; C. Solution 18; D. Solution 17.

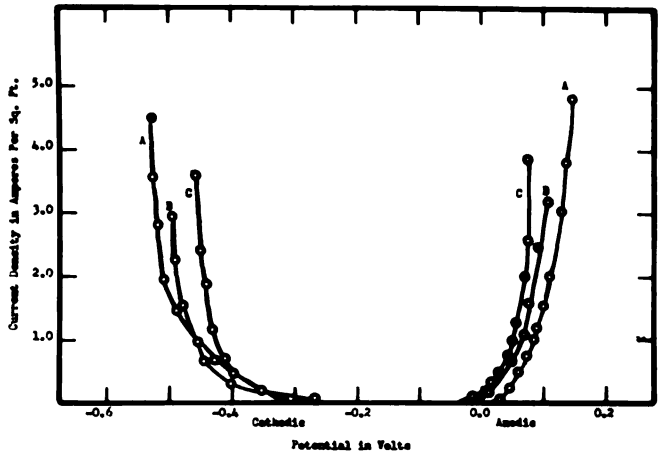

Fig.47. Current Density-Potential Curves at 50 C.(Hydrogen Cell Scale)

Curves: A. Solution 23; B. Solution 20; C. Solution 7.

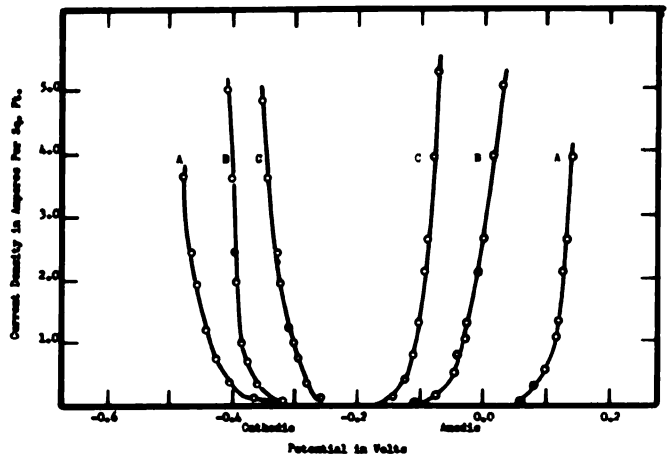

Fig.48. Current Density-Potential Curves(Hydrogen Cell Scale)

Curves: A. Solution 26 at 25°C; B. Solution 26 at 50°C; C. Solution 26 at 75°C.

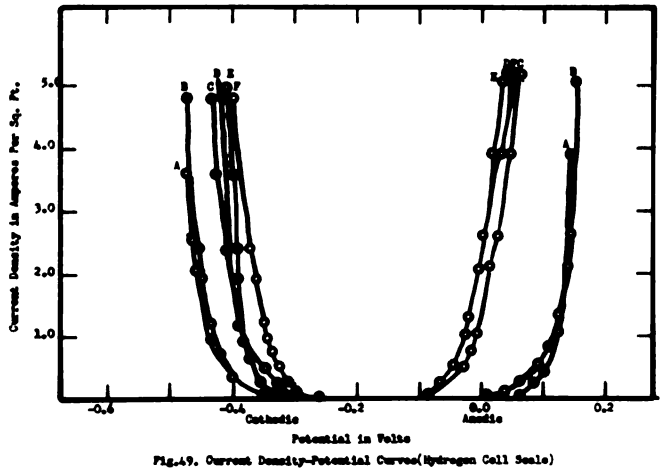

Fig.49. Current Density-Potential Curves(Hydrogen Cell Scale)

Curves: A. Solution 26 at 25°C; B. Solution 30 at 25°C; C. Solution 28 at 50°C; D. Solution 31 at 50°C
E. Solution 26 at 50°C; F. Solution 30 at 50°C.

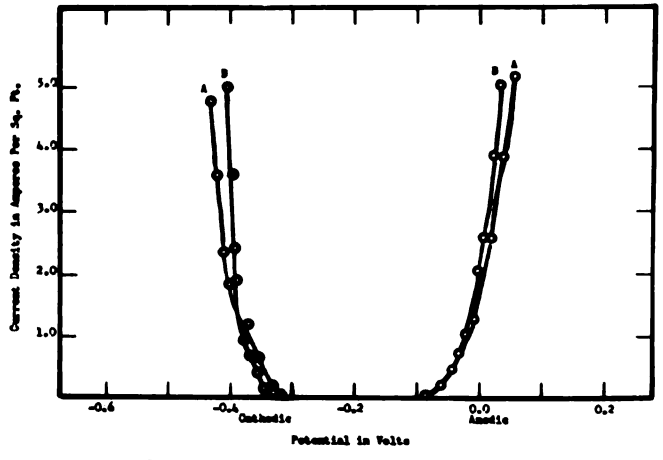

Fig.50. Current Density-Potential Curves(Hydrogen Cell Scale)at 50°C.

Curves: A. Solutions 32,33,or34; B. Solution 26.

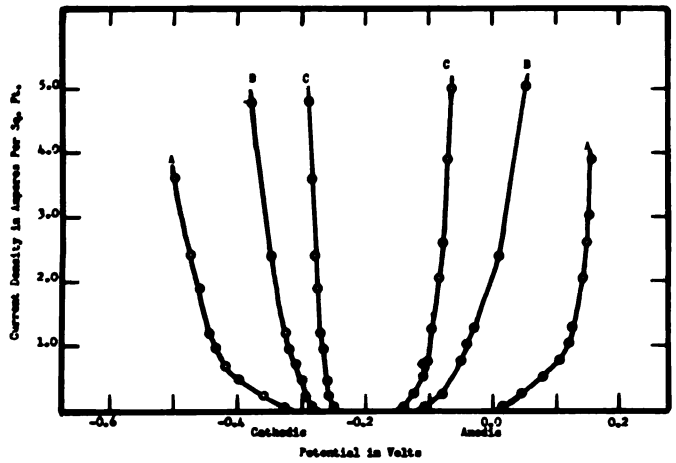

Fig. 51. Current Density-Potential Curves(Hydrogen Cell Scale)
Curves: A. Solution 1 at 25°C; B. Solution 1 at 50°C; C. Solution 1 at 75°C.

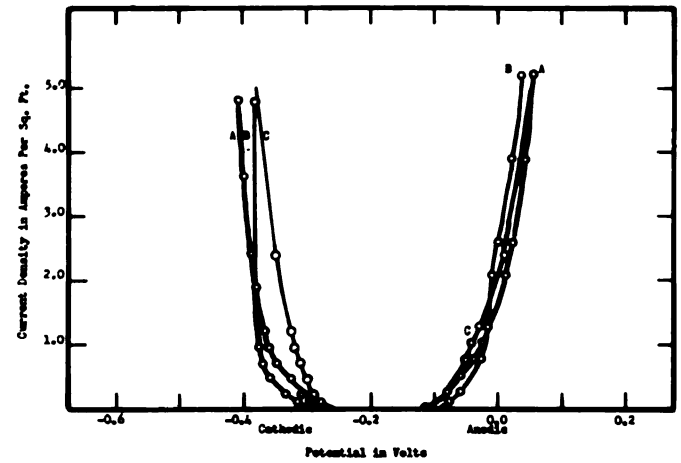

Fig. 52. Current Density-Potential Curves(Hydrogen Cell Scale)at 50°C.
Curves: A. Solution 4; B. Solution 2; C. Solutions 1 or 3;

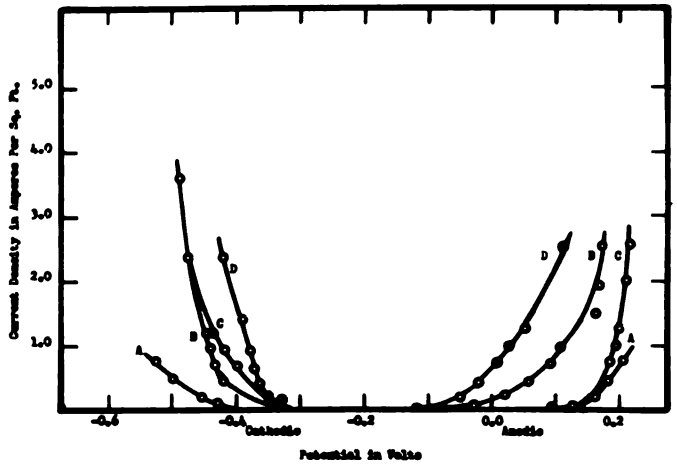

Fig. 53. Current Density-Potential Curves(Hydrogen Cell Scale)
Curves: A. Solution 5 at 25°C; B. Solution 5 at 50°C; C. Solution 6 at 50°C; D. Solution 5 at 75°C.

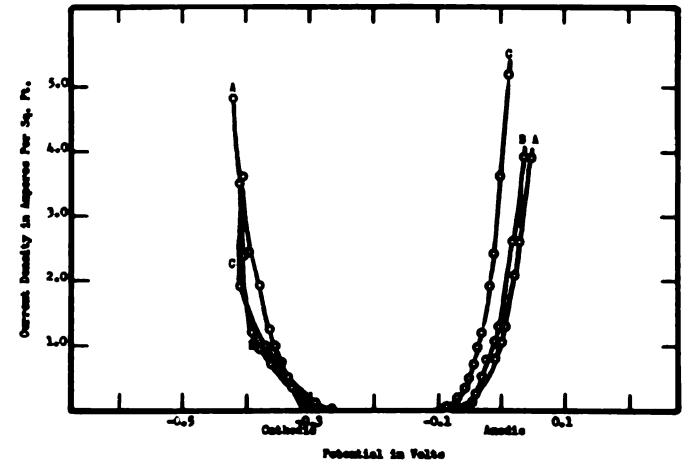

Fig. 54. Current Density-Potential Curves(Hydrogen Cell Scale)
Curves: A. Solution 9 at 75°C; B. Solution 12 at 75°C; C. Solution 7 at 75°C.

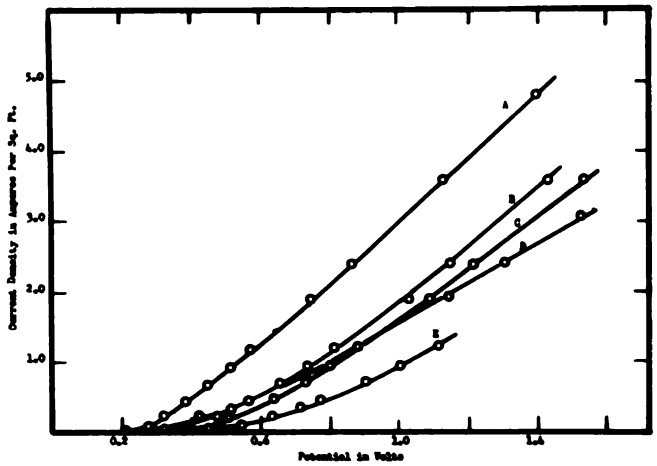

Fig.95.- Current Density-Cell Potential Curves

Curves: A. Solution 7 at 75°C; B. Solution 7 at 50°C; Solutions 12 or 9 at 50°C

D. Solution 11 at 50°C; E. Solution 11 at 25°C

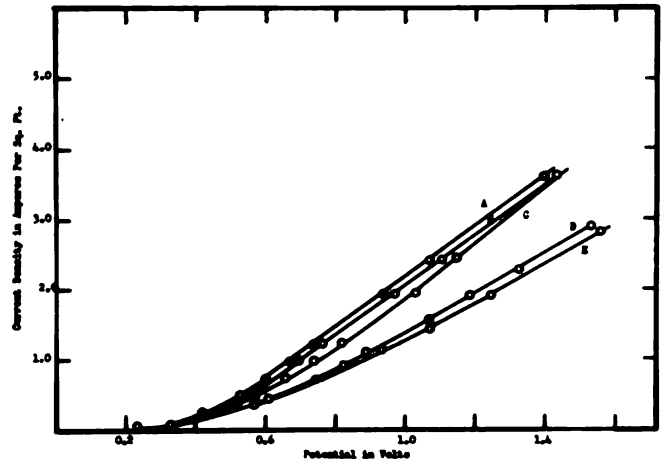

Fig.96. Current Density—Cell Potential Curves at 50°C

Curves: A Solution 17; B. Solutions 18 or 19; C. Solutions 7,14,15, or 16; D. Solution 20; E. Solution 21

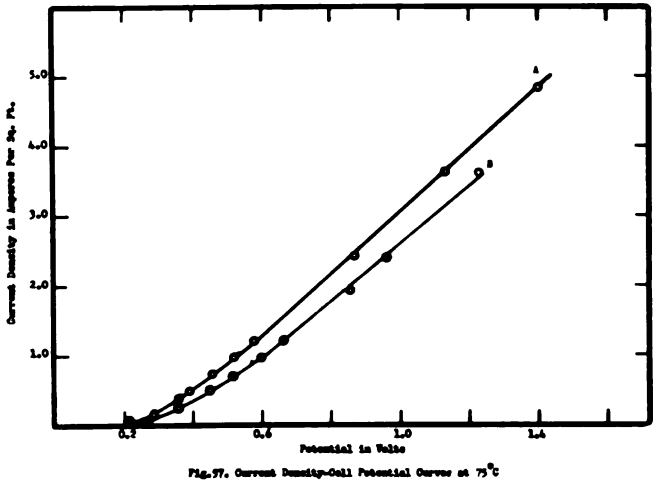

Fig.97. Current Density-Cell Potential Curves at 75°C

Curves: A. Solution 7; B. Solutions 9 or 12

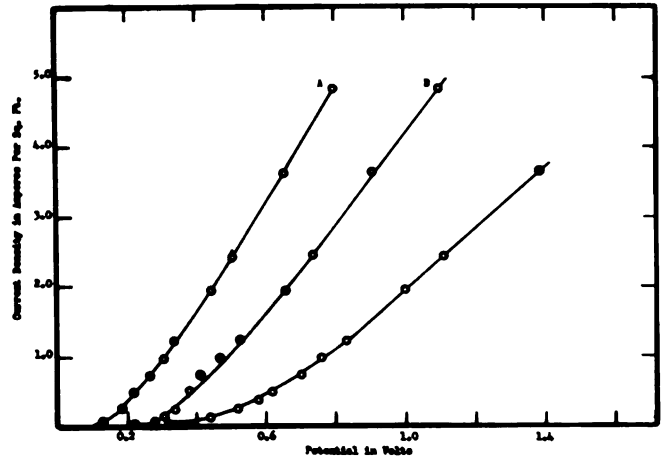

Fig.98. Current Density-Cell Potential Curves

Curves: A. Solution 26 at 75°C; B. Solution 26 at 50°C; C. Solution 26 at 25°C

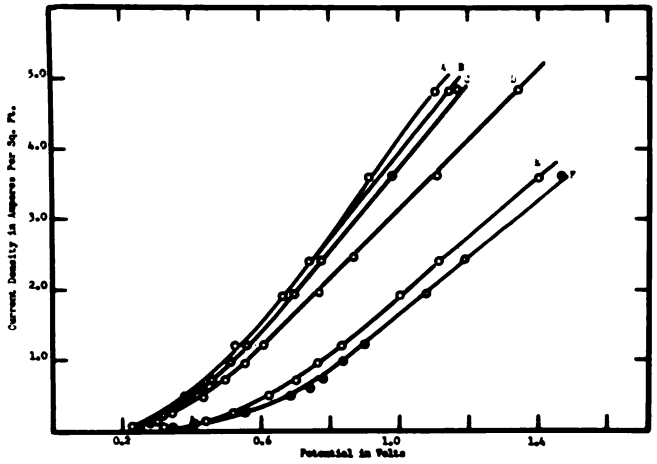

Fig.59. Current Density-Cell Potential Curves

Curves: A. Solution 26 at 90°C; B. Solution 30 at 90°C; C. Solution 31 at 90°C; D. Solution 28 at 90°C
E. Solutions 26 or 30 at 25°C; F. Solution 31 at 25°C

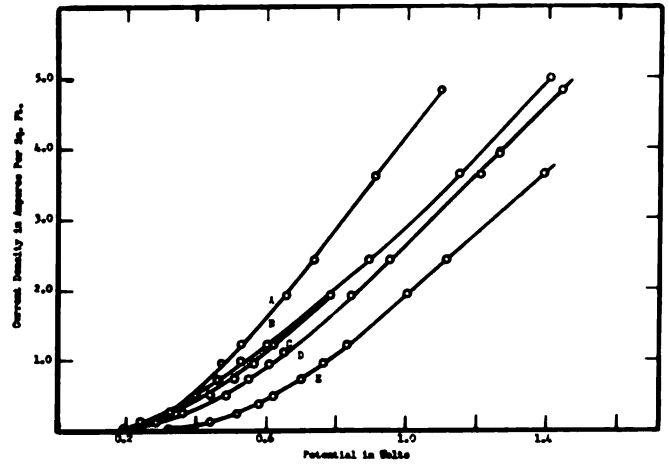

Fig.60. Current Density-Cell Potential Curves

Curves: A. Solution 26 at 90°C; B. Solution 32 at 90°C; C. Solution 33 at 90°C;
D. Solution 34 at 90°C; E. Solution 26 at 25°C

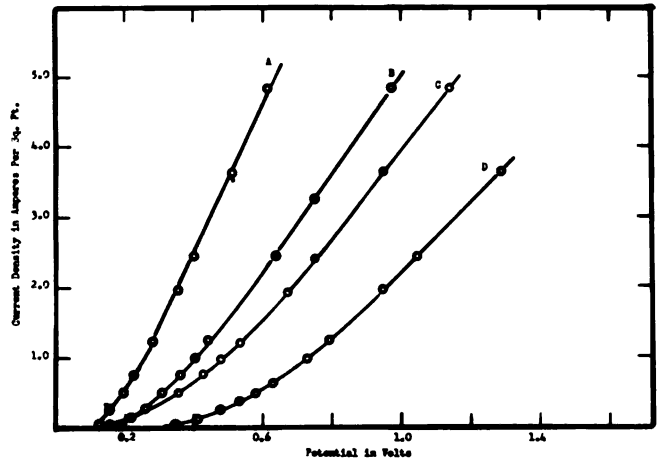

Fig.61. Current Density-Cell Potential Curves

Curves: A. Solution 1 at 75°C; B. Solution 1 at 50°C; C. Solutions 4 or 2 at 50°C; D. Solution 1 at 25°C

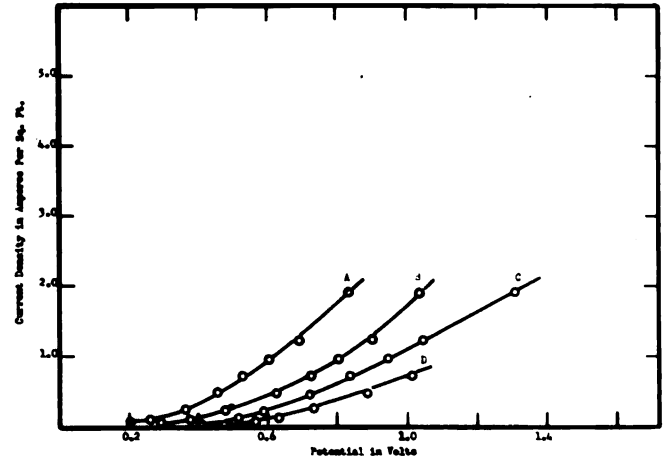

Fig.62. Current Density-Cell Potential Curves

Curves: A. Solution 5 at 75°C; B. Solution 5 at 50°C; C. Solution 6 at 50°C; D. Solution 5 at 25°C

DISCUSSION OF RESULTS

The reproducibility of potential curves obtained in this experiment is none too good. The values obtained depend upon several variables such as the variation in the roughness and structure of the anode and cathode with change in current density, the distance between the electrodes, and with variations in the convection currents in the vicinity of the electrodes. Furthermore, it is quite evident that the curves could be displaced considerably by a variation in the size of the cell or electrodes. However, since most of the variables were maintained constant throughout this investigation, the results should provide a good means for studying the comparative effects of the addition agents on current density - potential curves. It is to be understood, however, that no specific measurement can be considered as a constant reproducible value, for even with seemingly constant conditions, the author found that the results varied $\pm$ 15 - 20%.

The disucssion of this phase of the problem shall be concerned solely with an evaluation of the increase or decrease in the potential curves. As was mentioned in the introduction, the author has no intentions of explaining the curves in the light of other related plating problems.

In the following discussion it will be noted that the author mentions a decrease or increase in the anodic or cathodic curves. An increase in the cathodic curve signifies a shift to a more

negative potential, whereas an increase in the anodic curve signifies a shift to a more positive potential. A decrease in either curve indicates the exact opposite effect.

Watts Bath

Figure 43 merely shows the effect of temperature on the standard Watts bath (solution 7) and substantiates the already well known fact that an increase in temperature makes the cathodic curve less negative and the anodic curve less positive. Figure 44 indicates that the addition of benzene sulfonamide to the standard bath decreases the cathodic curve throughout the current density range. The anodic curve is also decreased above .5 amperes per sq. ft. Figure 44 also shows that the addition of sodium o-benzoyl sulfimide to the standard solution (curve B), or the addition of both Class I compounds to the standard bath (curve A) increase the cathodic and anodic curves at 50o C., with the effect of the latter compounds somewhat greater on the cathodic curve. Figure 54 shows that temperature is of some importance in discussing the effects of these addition agents on the potential curves. There is little significant difference in the comparative effect on the anode at 50° C. or at 75° C. Solution 12 containing both Class I addition agents has little effect on the cathodic curve at 75°C. whereas it caused a slight increase at 50° C. Solution 9 containing only sodium o-benzoyl sulfimide as an addition agent, slightly decreased the standard cathodic curve from .5 - 3.5 amperes per sq. ft. inclusive at 75° C. in contrast to the slight increase at 50°C.

This indicates that the polarization effect of the sodium o-benzoyl sulfimide at 50° C. is nullified by the increased temperature. Figure 55 shows that solution 9 and solution 12 increase the cell potential approximately the same, whereas solution 11 containing benzene sulfonamide increases the voltage at current densities above 1.5 amperes per sq. ft. Figure 45 clearly indicates that zinc has practically no effect on the curves. However, zinc in a concentration of .1 g./l. appears to have a very slight increasing effect on both the anode and cathode curves. Curve C, Figure 56, also shows that zinc has no effect on the cell potentials. The differences were too slight to graph, and thus it was convenient to show the effect of all three concentrations of zinc as one curve. Figure 46 indicates that the anodic and cathodic curves are decreased by the addition of benzene sulfonamide to zinc, and furthermore curves A and B, Figure 56, also show a decrease in cell voltage for any specific current density. Figure 47 (curve B) indicates that PQ increases both the anodic and cathodic curves, and this effect, especially on the cathode, is more pronounced than with the other addition agents investigated. Curve A further indicates that the addition of sodium o-benzoyl sulfimide and benzene sulfonamide to PQ increases both curves to a slight extent. The cell voltage is somewhat increased by the addition of PQ and slightly more so when the Class I addition agents are present, as can be

noted by inspecting curves D and E in Figure 56. The effect of these Class I compounds is also more noticeable with increase in current density.

High Chloride Bath

Figure 48, shows substantially the same effect of temperature on the standard High Chloride bath as was shown on the standard Watts bath in Figure 43. The anodic and cathodic curves of the former bath, however, are decreased over those of the latter at corresponding temperatures. An increase in temperature is, furthermore, directly related to a decrease in cell voltage as can be seen from an inspection of Figure 58. The addition of benzene sulfonamide to the standard bath has little effect at 25° C. as shown by curves A and B, Figure 49, but at 50° C., the cathodic curve is decreased somewhat at all current densities. Curves C and D, figure 49, also indicate that sodium o-benzoyl sulfimide alone or in combination with benzene sulfonamide tends to increase the cathodic curve. This is directly analogous to the effect shown by the same compounds in the Watts bath. Sodium o-benzoyl sulfimide increases the anodic curve, whereas little effect is noticed when benzene sulfonamide is also present. It is, thus, further seen that benzene sulfonamide has a tendency toward decreasing the curves. Zinc plus both Class I compounds increase the anode and cathode potentials above 1 ampere per sq. ft., but the concentration of zinc seemingly has no effect, as can

be seen by inspecting Figure 50. The cell voltage, is definitely increased for any current density, however, when zinc and the Class I compounds are present in the standard bath. Although the concentration of zinc is not too important, the higher concentration shows the greatest effect.

Chloride Bath

Figure 51 again substantiates the temperature effect on the potential curves. At 50° C. and 75° C., the cathodic potentials are decreased in comparison with the corresponding curves of the High Chloride bath. At 25° C., however, there is little noticeable difference. The anodic curves are approximately the same for both solutions. This fact is rather interesting because it seems logical to predict that the additional chloride should have an enhanced corrosive effect thus decreasing the anodic curves. The only plausible explanation is that the chloride ion has an optimum concentration in its effect on the anode, and this concentration is realized in the High Chloride bath. Curve C, Figure 52, shows that benzene sulfonamide has no effect on either the anode or cathode curves. Sodium o-benzoyl sulfimide or both Class I compounds together, curves B and A respectively, effect an increase in the cathodic curves, with the latter showing a somewhat greater effect above 2 amperes per sq. ft. and a lesser effect below this current density. The anode curve is increased by solution 4 containing both addition agents, whereas solution

2 containing sodium o-benzoyl sulfimide increases the potential below 1.5 amperes per sq. ft. and decreases it above this current density. The decreasing effect of the benzene sulfonamide thus appears to be limited in this all chloride bath to the lower current densities.

Sulfate Bath

The curves for the standard Sulfate bath in Figure 53 indicate clearly the necessity of the chloride ion in nickel solution. Data was not obtained at higher current densities because the high resistance of the bath caused the voltage to exceed the limit of the potentiometer at very low currents. The effect of temperature is the same in this bath as in all others investigated, but the anodic and cathodic curves are greatly increased over those of any other bath. The presence of both Class I addition agents decreased the cathodic curve below 2.5 amperes per sq. ft. and had little effect above. The anodic curve was increased quite a bit below 1 ampere per sq. ft.

CONCLUSIONS

It is apparent from the discussion and from an inspection of Figures 43-54 inclusive that the addition agents studied have little effect on the anodic and cathodic potentials. The inability of the author, as well as other investigators, to reproduce potential curves makes it difficult to establish any definite conclusions. However, in general, the addition agents show the following effects on the standard baths:

1. Benzene sulfonamide has little effect but has a tendency to decrease the anodic and cathodic curves.
2. Sodium o-benzoyl sulfimide, on the other hand, effects a slight increase in the potentials. The one exception was in the Watts bath at 75°C., where a slight decreasing effect was noticed.
3. The Class I addition agents together cause an increase in the potentials, but a somewhat less effect than when sodium o-benzoyl sulfimide is used alone.
4. Zinc, by itself, has the least effect of any addition agent investigated, causing practically no change in the standard bath potentials. The effect of concentration is also negligible.
5. A combination of zinc and benzene sulfonamide, however, effects a decrease in the anodic and cathodic potentials, illustrating once again the decreasing effect of the benzene sulfonamide.

Furthermore, this combination of addition agents is the only one that causes a decrease in cell voltage in the standard Watts bath.

6. Zinc is not used alone in the High Chloride bath but in combination with both Class I addition agents, it causes an increase in all potential measurements. Thus it is concluded that zinc has more of an effect in the High Chloride bath than in the Watts bath. Furthermore, in the former bath, an increase in concentration causes an increase in the cell voltage for any particular current density.
7. PQ increases the potential measurements more than any other one addition agent investigated. This effect, however, is further enhanced by combining with the Class I compounds.
8. The already well known temperature effect was substantiated in that an increase in temperature decreases the anodic and cathodic curves and decreases the voltage necessary to cause any specific current to flow across the cell. Furthermore, although no intensive temperature effect was studied, it is the opinion of the author that, in general, the addition agents behave similarily at any temperature.
9. Although not directly connected with this investigation, the author substantiated the effect of the chloride ion in reducing the abnormal anodic potential produced in a pure sulfate nickel bath.

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