THE ELECTROLYTIC SEPARATION OF IRON FROM CONCENTRATED SOLUTIONS OF NICKEL AND COBALT FOR THE ELECTROLYTIC DEPOSITION OF NICKEL

Thesis for the Degree of M. S.

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Walter Orville Dow, Jr.

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This is to certify that the

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The Electrolytic Separation of Iron
from Concentrated Solutions of Nickel
and Cobalt for the Electrolytic Deposition
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THE ELECTROLYTIC SEPARATION OF IRON FROM CONCENTRATED SOLUTIONS OF NICKEL AND COBALT FOR THE ELECTROLYTIC DEPOSITION OF NICKEL

By

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A THESIS

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I hereby gratefully acknowledge the help and guidance of Dr. D. T. Ewing in the completion of this work. I wish to thank the Hanson-VanWinkle-Munning Company whose grant of a fellowship made this research possible. I also wish to thank Donald D. Clark for his valuable assistance in analysis.

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INTRODUCTION

It has been known for some time that small amounts of iron will markedly affect an alloy deposit from a nickel cobalt solution for the electrodeposition of nickel. Not only the appearance but the ductility of the deposit are adversely affected. Since no literature directly applicable to electrolytic removal of metallic ions from concentrated nickel solutions has been so far advanced, only such information as chemical precipitation of iron in some salts was obtained from that source.[1]

In determining the course of study of the electrolytic separation of the iron from the nickel cobalt plating solution, such factors as the range of current density, type of cathode, temperature, and agitation were derived from commercial experience and applications of fundamental theory.

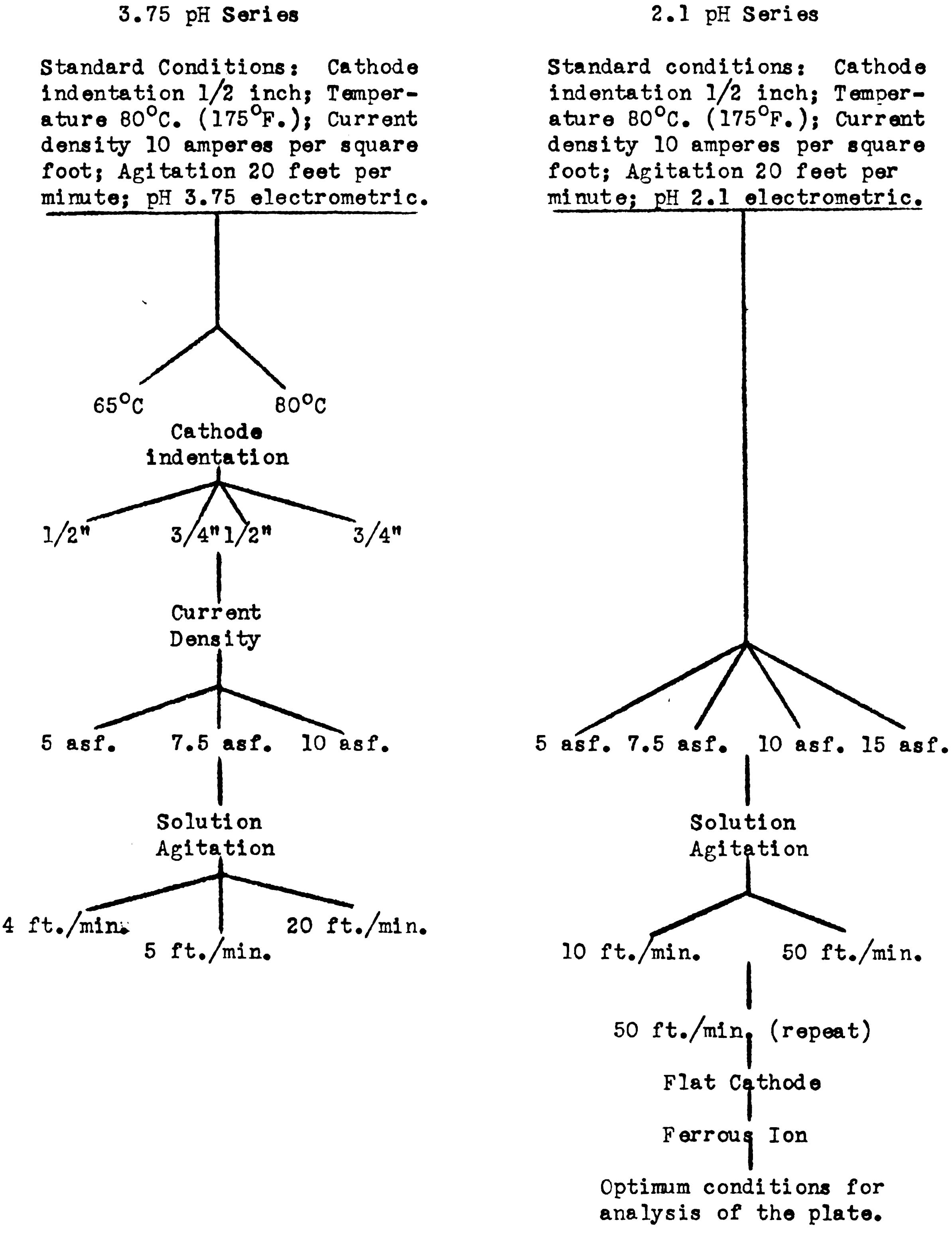
It was decided that an arbitrary set of standard conditions would be adapted and that each of the conditions would be varied in the succeeding experiments. As each condition was varied and evaluated, the optimum condition was used in all subsequent experiments.

These standard conditions were as follows: Agitation 20 feet per minute past the cathode; Current Density 10 ampers per square foot; Temperature 80.0° C. (175°F.); Cathode indentation 1/2 inch and a pH of 3.75 electrometric. Fernic sulphate ·7 HOH was used for contamination to give a ferric ion concentration of 100 milligrams per liter.

Figure A. shows the combination of conditions for each experiment.

For the 2.1 pH series of rate of removal experiments the best temperature and best cathode derived from the 3.75 pH series were accepted as optimum conditions and research was confined to variations of agitation, current density, and type of ion. (Ferrous rather than Ferric). One experiment was performed with a flat cathode. Experiments duplicating the conditions of the 50 feet per minute and optimum conditions experiments were also performed as checks.

FIGURE A.



3.75 pH Series

Standard Conditions: Cathode indentation 1/2 inch; Temperature 80°C. (175°F.); Current density 10 amperes per square foot; Agitation 20 feet per minute; pH 3.75 electrometric.

2.1 pH Series

Standard conditions: Cathode indentation 1/2 inch; Temperature 80°C. (175°F.); Current density 10 amperes per square foot; Agitation 20 feet per minute; pH 2.1 electrometric.

Optimum conditions for analysis of the plate.

Procedure- Solution preparation and purification.

3.75 pH Plating Solution

$NiSO_4$	32	oz./gal.	240	g./l.
$NiCl_2$	6	"	45	"
Boric acid	4	"	30	"
Ni Formate	6	"	45	"
$CoSO_4$	0.33	"	2.5	"
Ammonium Sulphate	0.33	"	2.5	"
Formaldehyde	0.33	"	2.5	"

2.1 pH Plating Solution

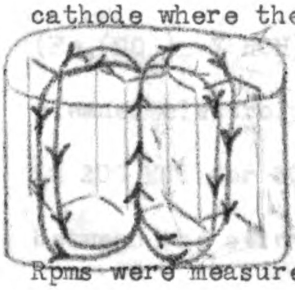
$NiSO_4$	32	oz./gal.	240	g./l.
$NiCl_2$	4	"	30	"
Boric acid	4.5	"	34	"
Ni Formate	4.5	"	34	"
$CoSO_4$	0.2-0.35	"	2.6	"

The plating solution was prepared with the amount of single nickel salts, nickel chloride and boric acid, omitting out cobalt sulphate and formaldehyde. After the salts had dissolved the pH was adjusted to 3.5-3.7 electrometric and the nickel formate then added. A slurry was prepared using one pound of filter aid with ten gallons of water per 100 gallons of plating solution and was spread over a filter paper on a suction filter flask. The bath was then filtered hot through activated charcoal slurry. (1 lb. charcoal to 100 gallons plating solution). The anodes were placed in the tank and cathodes of corrugated crimped sheet steel were hung from the cathode rod. The solution was electrolyzed at a current density of 5 amperes per square foot until 2-5 ampere hours per gallon had passed through the plating solution. The remaining salts were then added and the bath was ready for use.

Procedure- Rate of Removal Experiments on 1% NiCo Plating Bath.

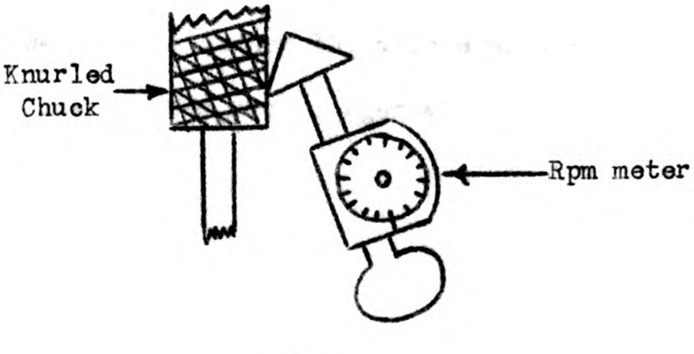
A 15 liter glass jar with 11.36 liters (3 gals.) of plating solution was set up on asbestos board insulation inside a water bath. Two stirring motors were placed so that the two shafts were at 1/4 and 3/4 of the tank diameter. Two stirrers were constructed with blades 1 cm. by 2 cm. tilted 45 degrees from the horizontal. For agitation greater than 20 feet per minute, stirrers were constructed with blades 1-3/4 cm. by 2-1/2 cm.

The blades were placed 5-1/2 inches below the surface of the bath, and lifted solution up from the bottom toward the top of the jar. The agitation, while reproducible, varies over the surface of the cathode. All agitation measurements were made at the edge of the cathode where the flow was most steady.



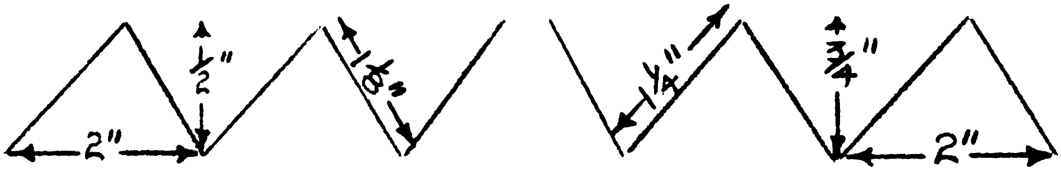
4 ft./min.	400-450 rpms.
5 ft./min.	600-650 rpms.
10 ft./min.	870-900 rpms.
20 ft./min.	1500 rpms.
50 ft./min.	1200 rpms. (with larger propellors)

Rpms were measured on the knurled part of the chuck for greater ease and accuracy. Chuck diameter was 11/16 inches.



The two corrugated cathodes were constructed from copper sheet to the following specifications:

8" x 11-5/8" with bends 1-1/8" apart for the 1/2" indentation
8" x 13-3/4" with bends 1-1/4" apart for the 3/4" indentation



The cathode was plated with a thin coat of nickel to prevent contamination of the bath by the exposed copper. A foot of heavy nickel wire was soldered to the cathode to lead completely away from the plating solution before other connections were made. Both anode hooks were plated heavily with nickel and 1% Nickel Cobalt anodes were placed against the sides of the jar behind the two stirrers. All connections leading from the bath were soldered to insure good connections. The bath was heated to temperature with stirrers going and 100 milligrams per liter of iron as ferric sulphate ($Fe_2(SO_4)_3 \cdot 7$ HCH) (8.57 g. per 3 gallons) were added. The cathode was cleaned electrolytically in boiling alkaline cleaner, rinsed, dipped in 20% HCl for 30 seconds, rinsed with distilled water, then placed between the stirrers at right angles to the line between the anodes. 1.23 square feet were submerged. The time was checked and a 5 ml. sample taken, numbered and saved for analysis. Samples were taken at intervals which were short (every 100 ampere minutes per gallon) at the beginning of the run and much longer at the end of the run.

(Every 1000 ampere minutes per gallon.) The pH was checked at each sample and if necessary, lowered with sulphuric acid or raised with nickel carbonate. The samples were analyzed for iron and plotted with iron content against ampere minutes per gallon.

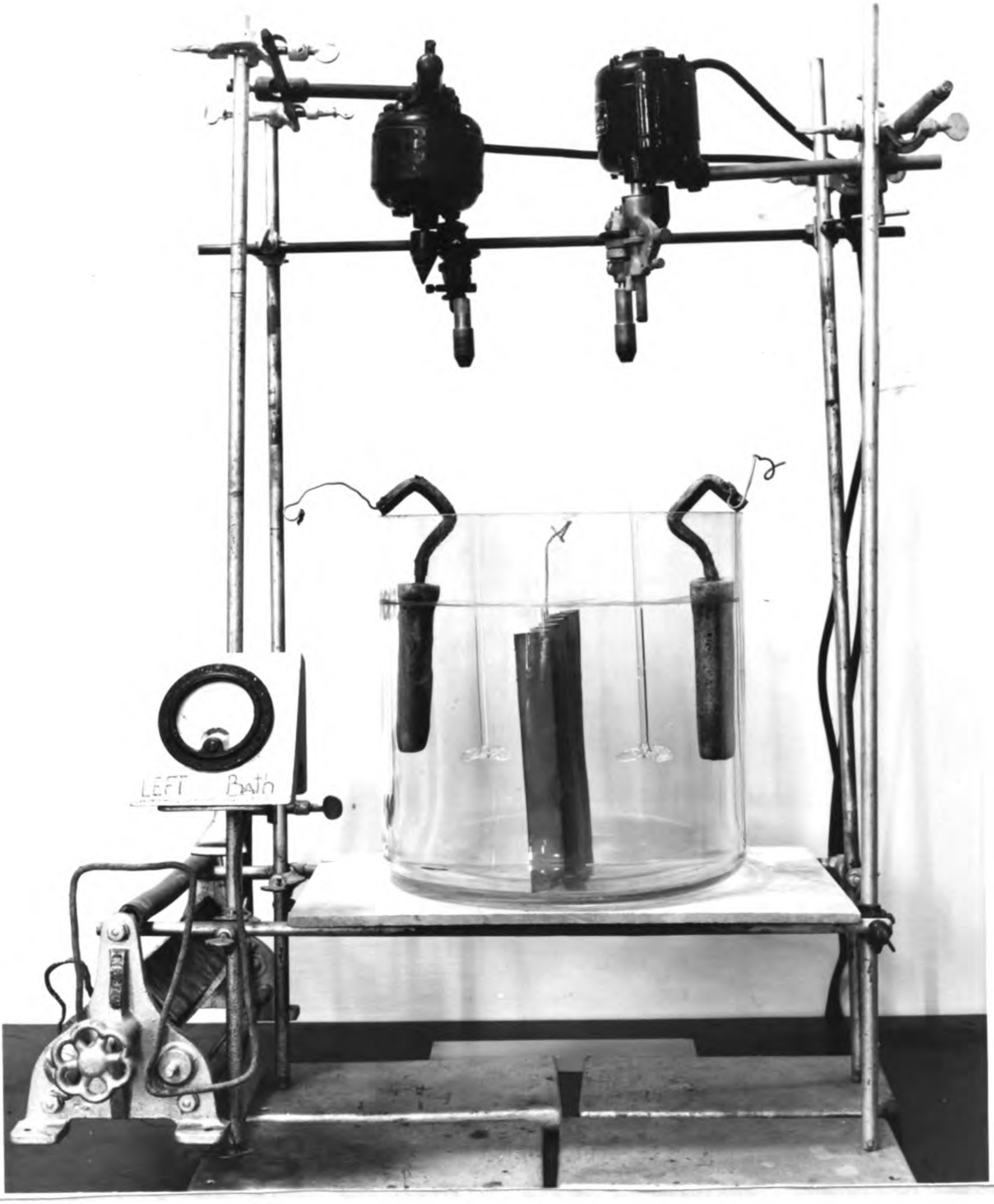


Fig. B. Apparatus for Rate of Removal Runs on a 1% (9H) NiCo Plating Solution.

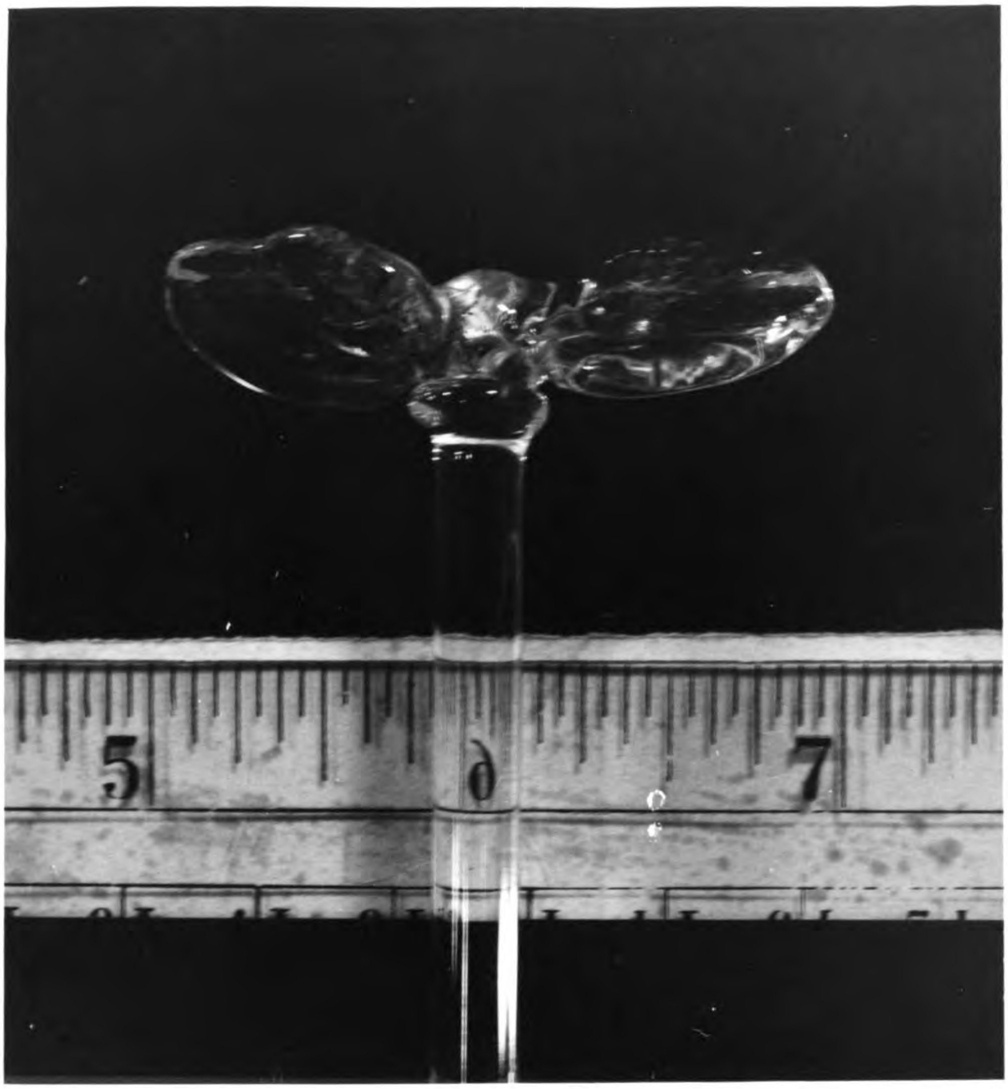


Fig. C. Large stirring propellor used in 50 ft. per min. agitation.

Analysis of Iron-
Separation of the Iron.

(1) Add enough chopped distilled water ice to fill a 100 ml. separatory funnel one third.

(2) Add 2 ml. nickel plating solution.

(3) Add 4 ml. ice cold cupferron. (1% solution.) (Make up fresh every day)

(4) Shake 1 minute and let stand for 10 minutes. Do not shorten this standing period.

(5) Add 5 ml. amyl acetate from a burette. Shake 1 minute, allow liquid layers to separate and draw off aqueous layer into another separatory funnel.

(6) Repeat twice with 5 ml. portions of amyl acetate. If an amber color persists in this last extraction use a smaller amount of nickel plating solution for a sample.

(7) Combine amyl acetate extracts and wash with 10 ml. of water. Shake 1 minute and discard the aqueous layer.

Isolation of the Fe.

(8) Add 4 ml. nitric acid (1:1). Shake 2 minutes or until the yellow color disappears. (This has taken as long as 10 minutes.) Run aqueous layer into a 100 ml. volumetric flask.

(9) Shake amyl acetate layer with 10 ml. water. Run aqueous layer into volumetric flasks. The amyl acetate should be light green in color.

(10) Now add in succession with mixing in between additions, 6 ml. hydroxylamine hydrochloride, 2 ml. o-phenanthroline and 20 ml. of 40% sodium acetate.

(11) Dilute to the mark with redistilled water and mix well.

(12) Using a test tube partially full of water as the reference liquid, adjust the colorimeter so that the galvanometer pointer is set at zero when the dial reading is at zero. Use the green #54 filter.

(13) Rinse the test tube with small amount of colored solution and fill to the mark with sample.

(14) Put the tube in the colorimeter (Klett-Somerson) and flip side switch on. Adjust dial to make galvanometer needle hit zero, then read dial.

(15) Run a blank following the above procedure exactly <u>except</u> for adding the o-phenanthroline.

(16) Subtract the blank from the scale reading and read milligrams per liter of iron from the calibration curve.

<u>Note</u>* This procedure was worked out from results obtained using the method proposed by Serfass and Levine, Leheigh University. Recognizing the fact that coloration of amyl acetate portions in excess of the extractions used by Serfass and Levine indicated more iron to be gotten out and that the curve at higher concentrations of iron was not showing high enough colorimetric readings to make it a straight line function, more extractions of amyl acetate were added, color changes stressed as end points in shaking and extraction, and double quantities of sample and most reagents were used to insure greater accuracy. Result: straight line calibration curve and highly reproducible results.

EXPERIMENT NUMBER X1

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Run
1	41	132	Agitation 20 ft./min.
2			Current density 10 asf.
3	250	128	Cathode indentation 1/2 in.
4	500	126	Temperature 80°C. (175° F.)
5	1125	100	Contamination 100 mg./l. Fe^{+++}
6	1500	80	(8.57 grms. $Fe_2(SO_4)_3$ per 3 gal.)
7	1700	76	pH 2.1
8	2500	65	
9	3500	52	
10	4250	39	
11	5000	30	At 6875 amp. min./gal. a nickel
12	5375	30	plated copper cathode was in-
13	6227	30	serted in place of the nickel
14	6875	28	plated steel cathode used in the
15	7195	26½	
15a	7195	24	
16	7695	23	
17	8687	22	
18	9302	23	

EXPERIMENT NUMBER X2

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Run
1	0	120	Agitation 20 ft./min.
2	368	113	Current Density 7.5 asf.
3	1008	103	Cathode Indentation 1/2 in.
4	2200	90	Temperature 80°C. (175° F.)
5	2997	78	Contamination 100 mg./l Fe^{+++}
6	4606	63	pH 2.1
7	5711	56	
8	6631	47	At 5000 amp.min./gal. the plate
9	7750	43	was stripped of all peeling Ni,
10	9053	36	cleaned electrolytically, ethched
11	9636	36	and the run was begun again.

EXPERIMENT NUMBER X3

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0		Agitation 20 ft./min.
2	246		Current Density 5 asf.
3	492		Cathode Indentation 1/2 in.
4	984	123	Temperature 80°C. (175° F.)
5	1968	112	Contamination 100 mg./l. Fe^{+++}
6	2952	107	pH 2.1
7	3936	90	
8	4920	79	
9	6930	60	
10	8562	66	
11	10918	65	

EXPERIMENT NUMBER X4

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	133	Agitation 10 ft./min.
2	246		Current Density 10 asf.
3	492	127	Cathode Indentation 1/2 in.
4	984		Temperature 80°C. (175° F.)
5	1620		Contamination 100 mg./l. Fe^{+++}
6	2870	87	pH 2.1
7	3936	81	
8	5904	78	

EXPERIMENT NUMBER X5

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	135	Agitation 20 ft./min.
2	185	122	Current Density 15 asf.
3	369	108	Cathode Indentation 1/2 in.
4	955	95	Temperature 80°C. (175° F.)
5	1107		Contamination 100 mg./l. Fe^{+++}
6	1476	89	pH 2.1
7	1845	70	
8	2583	52	
9	3750	47	
10	4797	46	

EXPERIMENT NUMBER X6

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	144	Agitation 50 ft./min.
2	348	127	Current Density 10 asf.
3	492		Cathode Indentation 1/2 in.
4	738	103	Temperature 80°C. (175° F.)
5	984	65	Contamination 100 mg./l. Fe^{+++}
6	1476	69	pH 2.1
7	1968	69	
8	2952	58	
9	3608	62	
10	5100	45	

EXPERIMENT NUMBER X7

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	99	Agitation 50 ft./min.
2	246	84	Current Density 10 asf.
3	492	--	Cathode Indentation 1/2 in.
4	738	59	Temperature 80°C. (175° F.)
5	984	50	Contamination 100 mg./l. Fe^{+++}
6	1476	65	pH 2.1
7	1570	61	
8	2062	58	
9	2800	50	Values plotted were the average
10	3784	57	of two analysis.
11	4522	55	

EXPERIMENT NUMBER X8

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	107	Agitation 20 ft./min.
2	246	98	Current Density 10 asf.
3	492	82	Cathoded Indentation Flat
4	738	72	Temperature 80°C. (175° F.)
5	984	70	Contamination 100 mg./l. Fe^{+++}
6	1189	61	pH 2.1
7	1189	65	
8	1435	47	
9	1927	54	
10	3054	43	
11	3054	48	
12	4038	42	
13	4653	41	

EXPERIMENT NUMBER X9

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	75	Agitation 20 ft./min.
2	246	69	Current Density 10 asf.
3	492	50	Cathode Indentation 1/2 in.
4	615	69	Temperature 80°C. (175° F.)
5	738	47	Contamination 100 mg./l. Fe^{++}
6	738	47	pH 2.1
7	984	52	
8	1230	62	Averages of two or more
9	1415	52	analysis were used in plotting.
10	1907	54	There were 8-10 mg./l of ferric
11	2599	50	iron left in the bath when the
			ferrous iron was added.

EXPERIMENT NUMBER X10

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	98	Agitation 20 ft./min.
2	246	75	Current Density 10 asf.
3	492	70	Cathode Indentation 1/2 in.
4	738	74	Temperature 80°C. (175° F.)
5	984	45	Contamination 100 mg./. Fe^{+++}
6	1230	48	pH 2.1
7	1476	38	
8	1722	36	Copper Cathode was plated with
9	1968	--	nickel, then oxidized in alkaline
10	2460	32	cleaner for 15-30 secs. Rinsed in
11	2952	35	distilled water and replaced in
12	3444	33	plating bath.
13	3936	--	

EXPERIMENT NUMBER X11

Sample Number	Hours	Mg./l. Iron	Conditions of the Experiment.
1	0	127.5	Agitation 20 ft./min.
2	1	127.5	Temperature 80°C. (175° F.)
3	3	128	pH 2.1
4	4	125	Contamination 100 mg./l. Fe^{+++}
5	20	130	Sample number 5 was taken the next day after the solution had cooled. Agitation only was used.

EXPERIMENT NUMBER XX1

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	115	Agitation 20 ft./min.
2	246	--	Current Density 10 asf.
3	492	56	Cathode Indentation 1/2 in.
4	738	--	Temperature 65°C. (150° F.)
5	984	36	Contamination 100 mg./l. Fe^{+++}
6	1476	--	pH 3.75
7	1968	35	
8	2766	29	Solution was filtered hot at the end of the experiment.
9	3444	--	
10	4774	--	
11	5166	26	

EXPERIMENT NUMBER XX2

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	66	90	This experiment is a combination of two; One from 90 mg./l. to 12 mg./l. and the other from 12mg./l. to 9 mg./l. Agitation 20 ft./min. Current Density 10 asf. Cathode Indentation 1/2 in. Temperature 80^{o}C. (175^{o} F.) Contamination 100 mg./l. Fe^{+++} pH 3.75 This experiment was performed in a $1\frac{1}{2}$ gal. battery jar.
2	150	$89\frac{1}{2}$	
3	344	55	
4	552	52	
5	676	25	
6	1352	12	
7	1800	10	
8	2260	9	

EXPERIMENT NUMBER XX3

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	83	Agitation 20 ft./min. Current Density 10 asf. Cathode Indentation 3/4 in. Temperature 80^{o} C. (175^{o} F.) Contamination 100 mg./l. Fe^{+++} pH 3.75
2	246	49	
3	492	27	
4	738	34	
5	984	--	
6	1353	17	
7	2275	--	
8	3198	10	
9	4182	6	

EXPERIMENT NUMBER XX4

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	100	Agitation 20 ft./min.
2	244	53	Current Density 5 asf.
3	488	30	Cathode Indentation 1/2 in.
4	732	26	Temperature 80° C. (175° F.)
5	976	23	Contamination 100 mg./l. Fe^{+++}
6	1952	18	pH 3.75
7	2928	17	

EXPERIMENT NUMBER XX5

Sample Number	Amp.min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	119	Agitation 20 ft./min.
2	184	74	Current Density 7.5 asf.
3	797	32	Cathode Indentation 1/2 in.
4	1288	22	Temperature 80° C. (175° F.)
5	2085	14	Contamination 100 mg./l. Fe^{+++}
			pH 3.75

EXPERIMENT NUMBER XX6

Sample Number	Amp.min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	102	Agitation 10 ft./min.
2	246	70	Current Density 10 asf.
3	492	53	Cathode Indentation 1/2 in.
4	738	46	Temperature 80°C. (175° F.)
5	984	37	Contamination 100 mg./l. Fe^{+++}
6	1476	27	pH 3.75
7	1676	27	
8	2496	16	This table is a combination of 2 experiments, one from 102 to 27 mg./l. and the other from 27 to 2 mg./l.
9	3558	9	
10	4476	4	
11	5476	2	

EXPERIMENT NUMBER XX7

Sample Number	Amp.Min. Per Gal.	Mg./l. Iron	Conditions of the Experiment.
1	0	92	Agitation 5 ft./min.
2	200	56	Current Density 10 asf.
3	1020	40	Cathode Indentation 1/2 in.
4	2082	12½	Temperature 80° C. (175° F.)
5	3033	8	Contamination 100 mg./l. Fe^{+++}
6	4000	4	pH 3.75
			Formic Acid was used to lower pH.

EXPERIMENT NUMBER XX8

Sample Number	Hours	Mg./l. Iron	Conditions of the Experiment
1	0	102	Agitation 80 ft./min.
2	1	62	Temperature 80°C. (175° F.)
3	3½	27	Contamination 100 mg./l. Fe^{+++}
4	4½	35	pH 3.75
5	6¼	20	
6	7½	--	

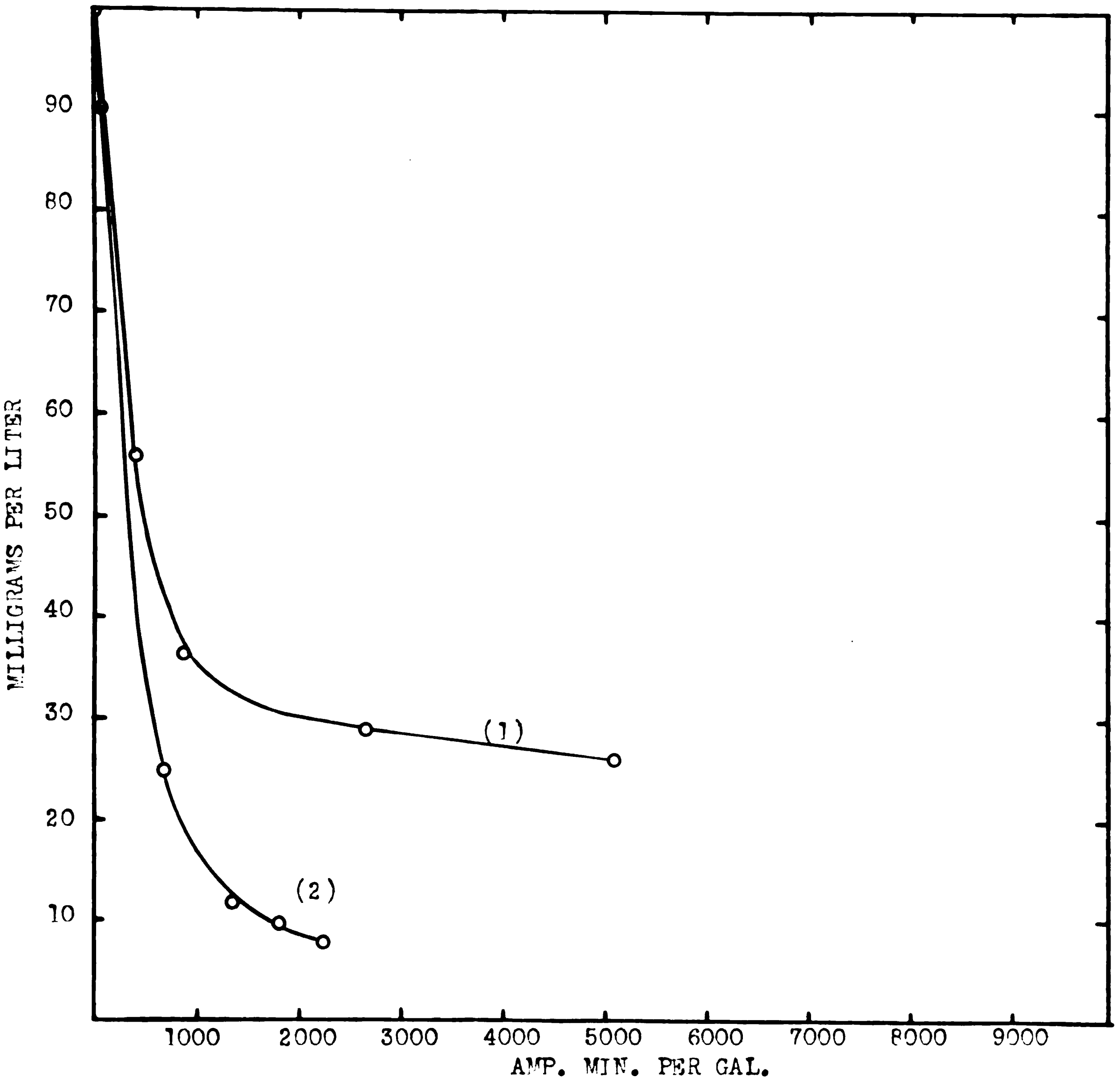


Fig. 1. Effect of Temperature on the Electrolytic Removal of Iron from a 3.75 pH NiCo (9H) Plating Solution.
Curve 1 - 150°F; Curve 2 - 175°F.

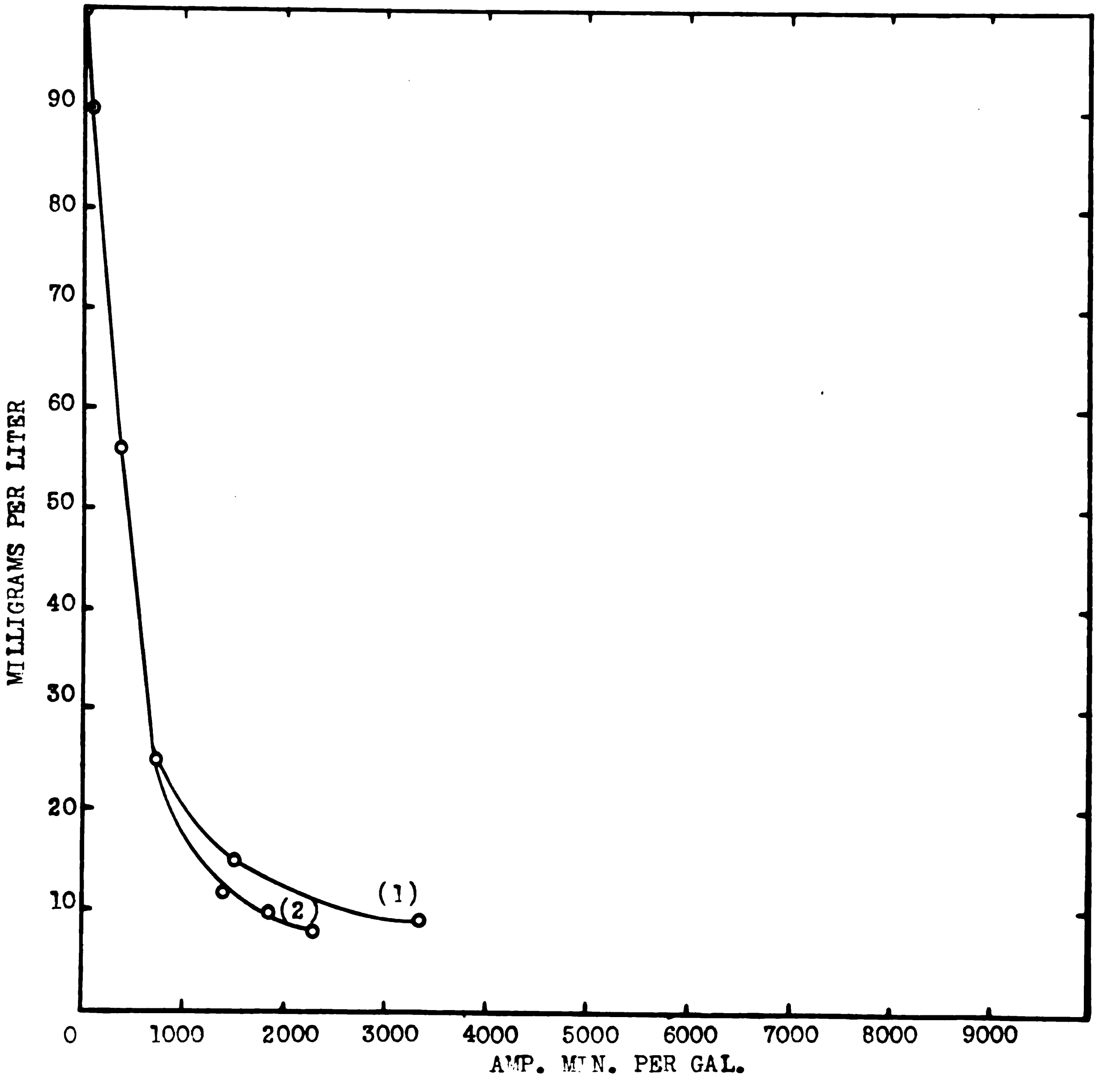


Fig. 2. Effect of Depth of Cathode Indentation on the Electrolytic Removal of Iron from a 3.75 pH NiCo (9H) Plating Solution.
Curve 1 - 3/4 in. Indentation; Curve 2 - 1/2 in. Indentation.

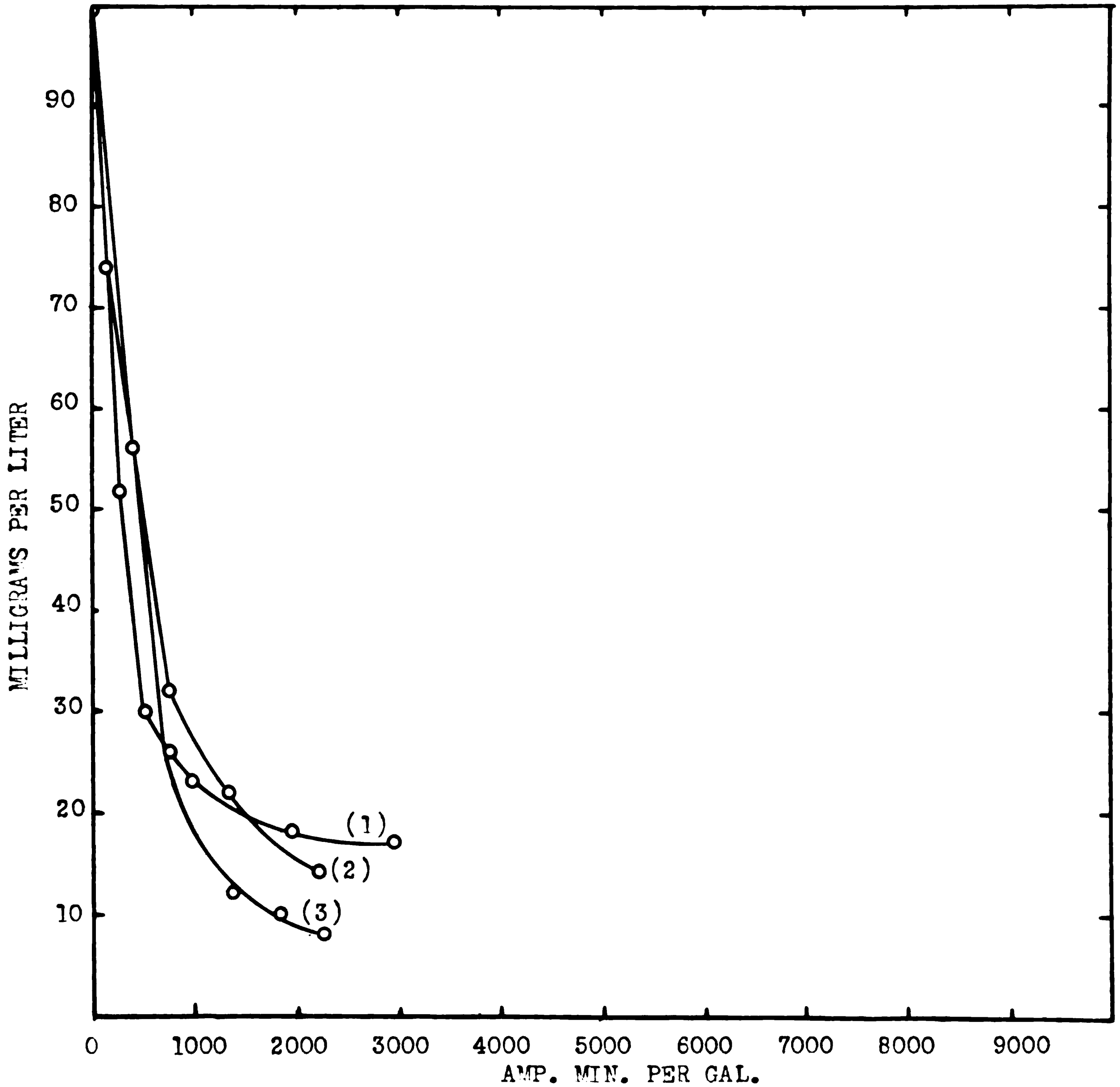


Fig. 3. Effect of Current Density on the Electrolytic Removal of Iron from a 3.75 pH NiCo (9H) Plating Solution.
Curve 1 - 5 amps per ft.^{2}; Curve 2 - 7-1/2 amps per ft.^{2}; Curve 3 - 10 amps per ft.^{2}.

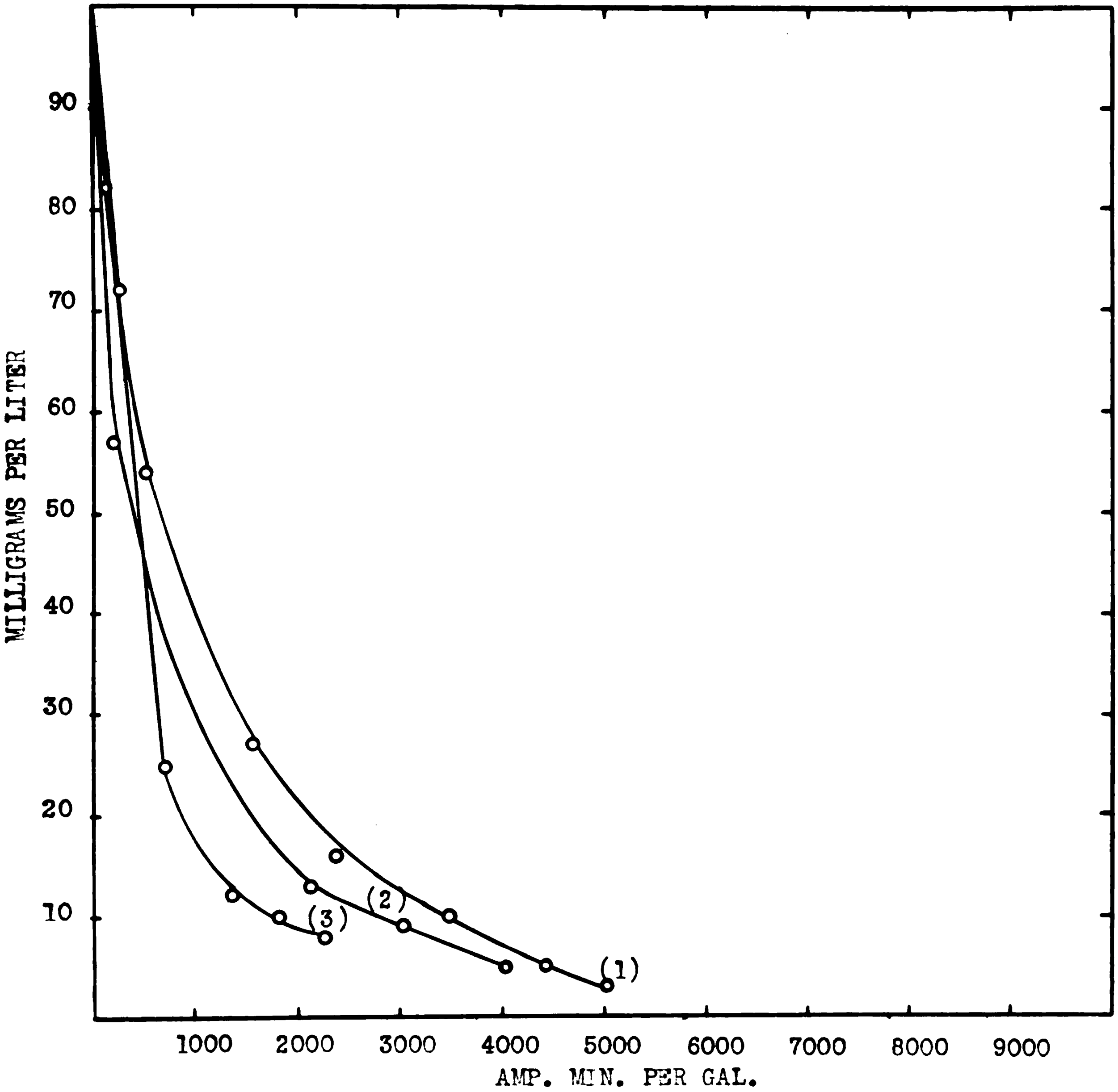


Fig. 4. Effect of Agitation on the Electrolytic Removal of Iron from a 3.75 pH NiCo (9H) Plating Solution.
Curve 1 - 4 ft. per min. past the Cathode; Curve 2 - 5 ft. per min. past the Cathode; Curve 3 - 20 ft. per min. past the Cathode.

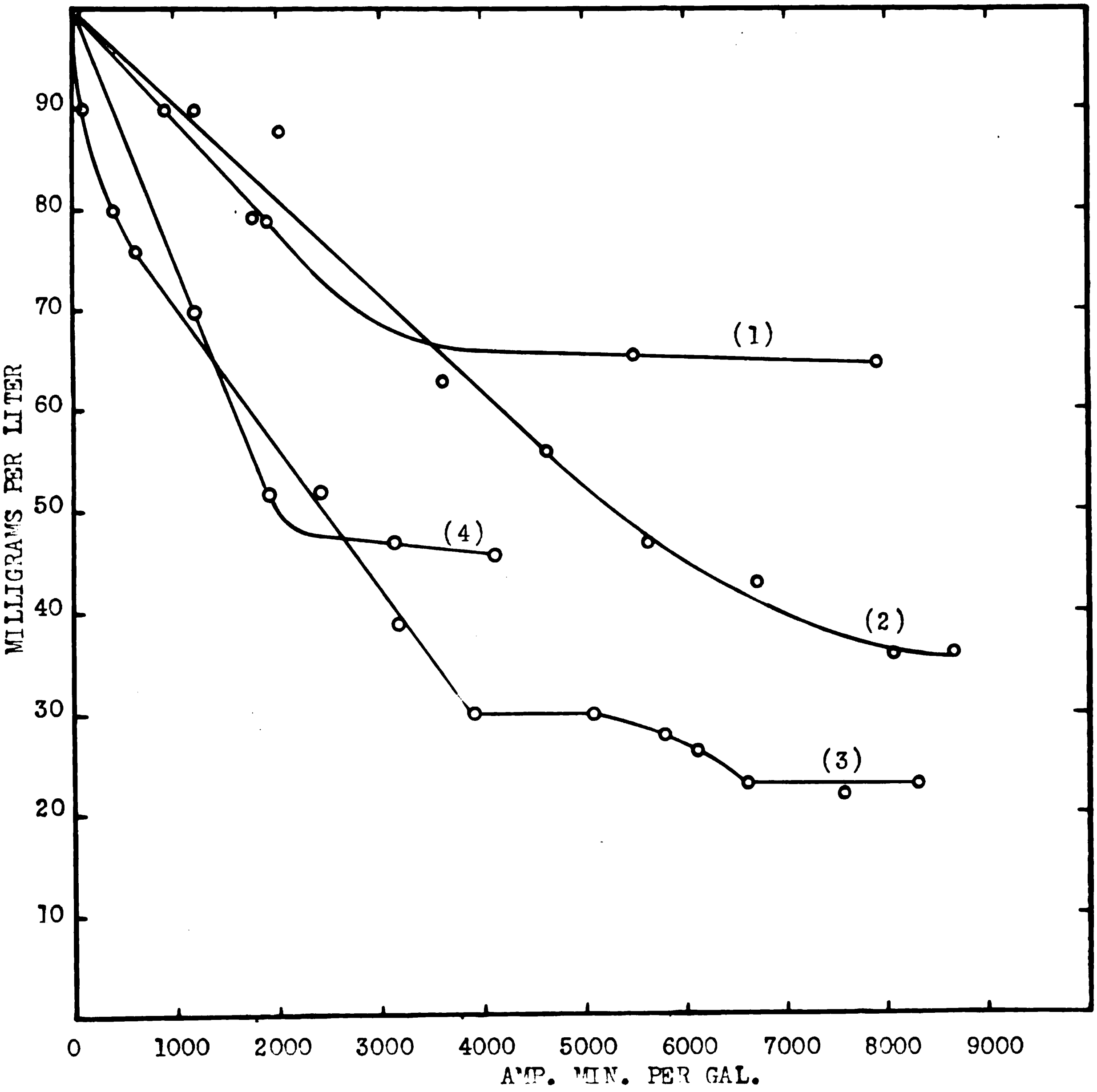


Fig. 5. Effect of Current Density on the Electrolytic Removal of Iron from a 2.1 pH NiCo (9H) Plating Solution. Curve 1 - 5 amps per ft.^{2}; Curve 2 - 7-1/2 amps per ft.^{2}; Curve 3 - 10 amps per ft.^{2}; Curve 4 - 15 amps per ft.^{2}.

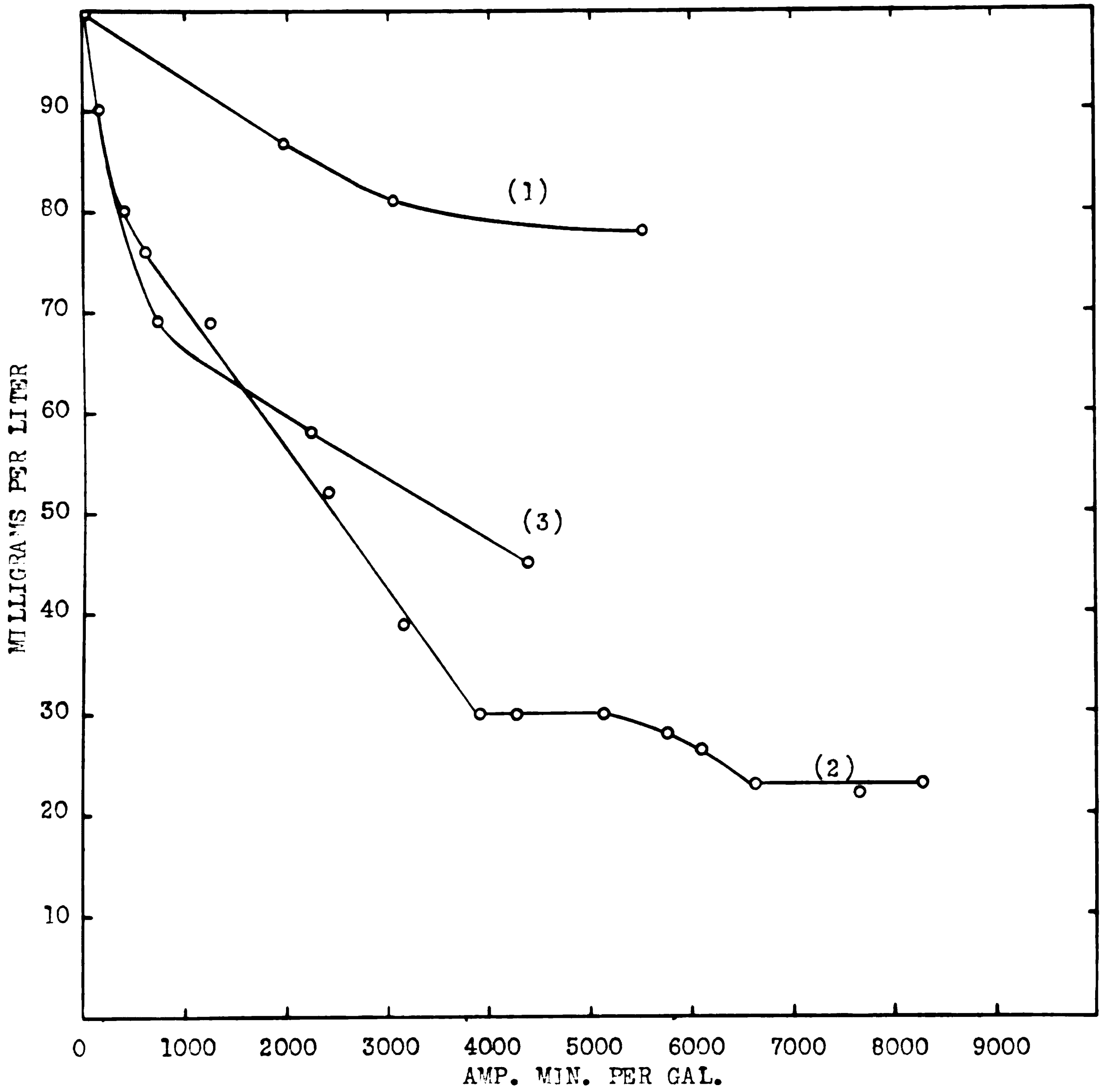


Fig. 6. Effect of Solution Agitation on the Electrolytic Removal of Iron from a 2.1 pH NiCo (9H) Plating Solution. Curve 1 - 10 ft. per min. past the Cathode; Curve 2 - 20 ft. per min. past the Cathode; Curve 3 - 50 ft. per min. past the Cathode.

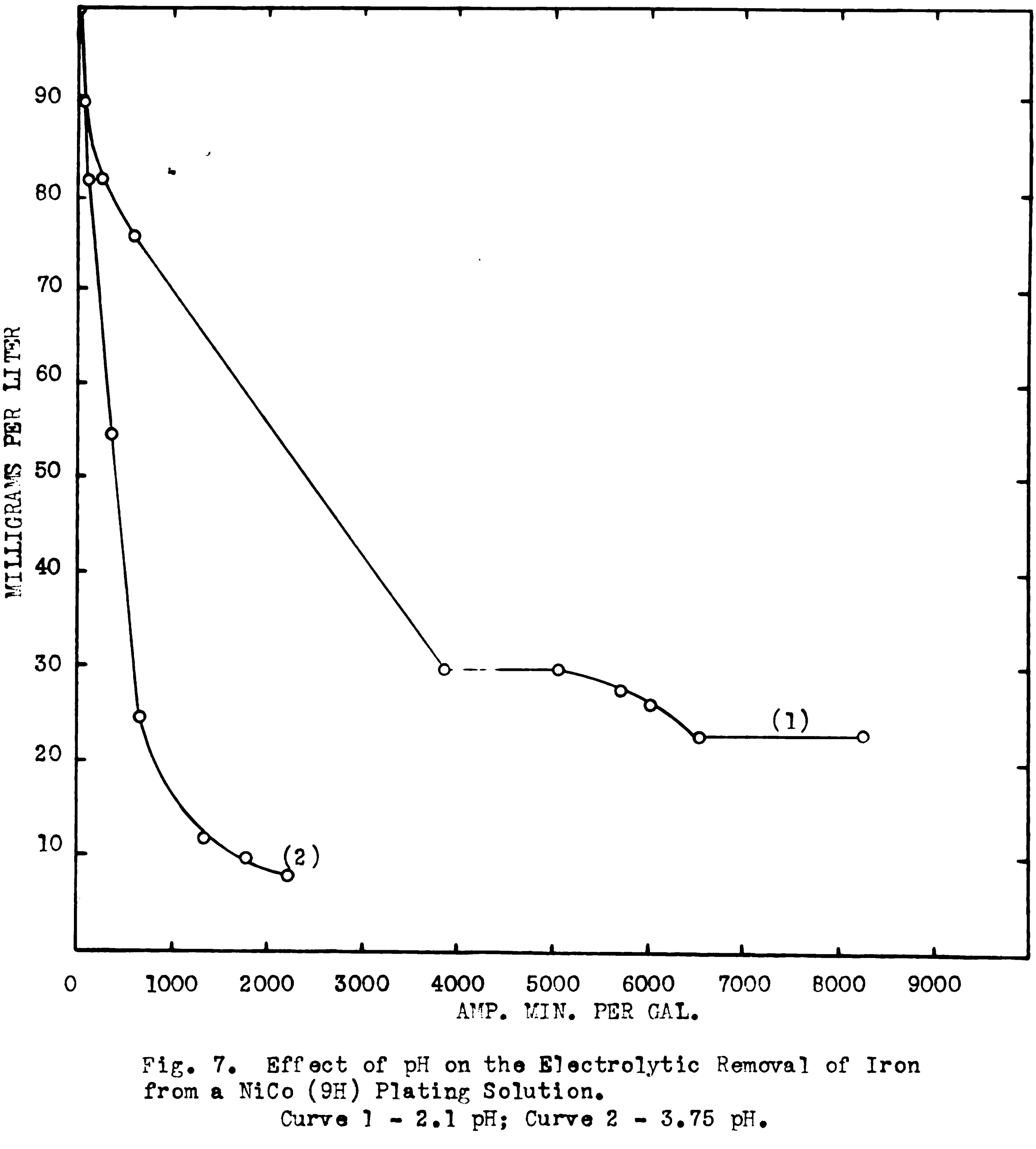


Fig. 7. Effect of pH on the Electrolytic Removal of Iron from a NiCo (9H) Plating Solution.
Curve 1 - 2.1 pH; Curve 2 - 3.75 pH.

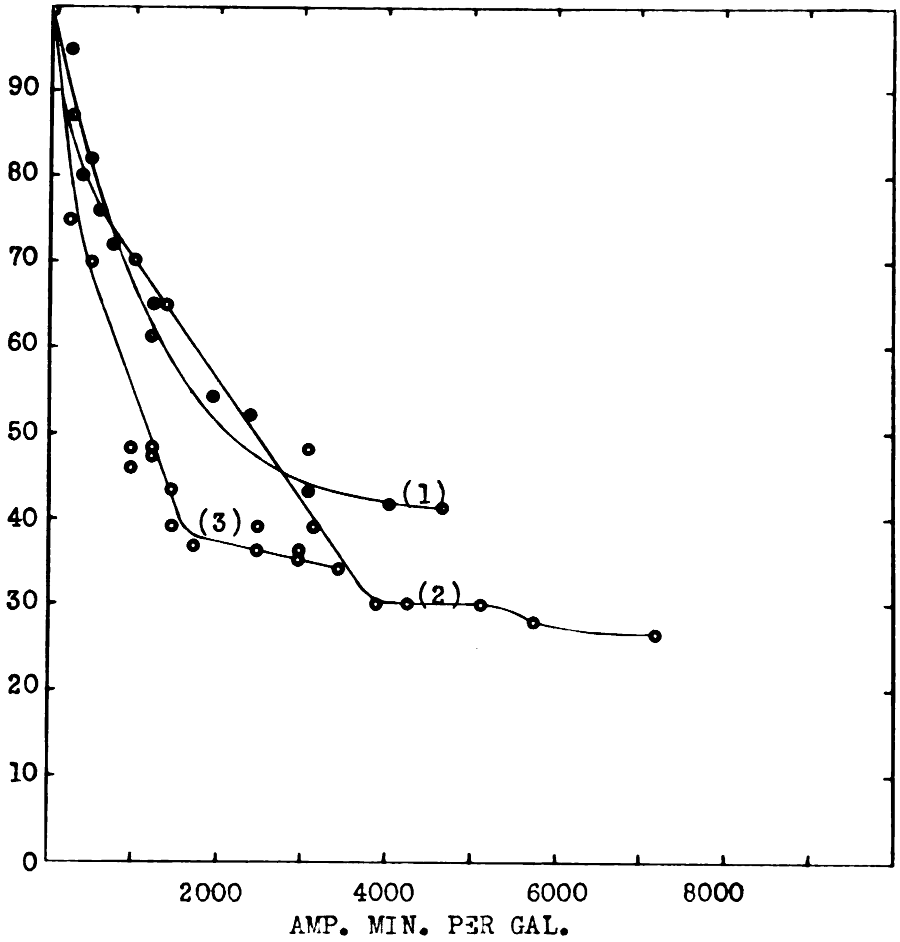


Fig. 8. The Effect of a Flat Cathode and a repeat experiment of Optimum Conditions Using a Copper Base Cathode.
Curve 1. Flat Cathode. Curve 2. Optimum conditions (steel base cathode). Curve 3. Optimum Conditions (copper base cathode).

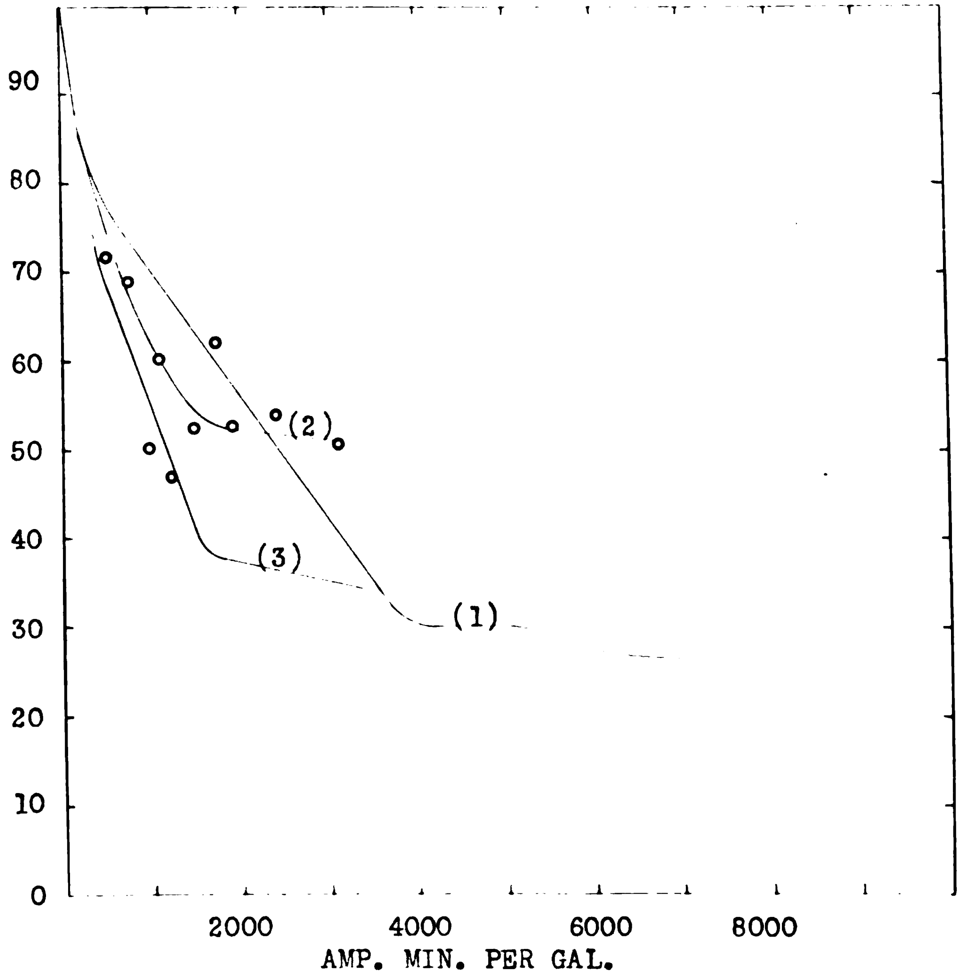


Fig. 9. The Rate of Removal of Ferrous iron from a 2.1 pH 1% Nickel Cobalt Solution.
Curve 1. Ferric iron (steel base cathode)
Curve 2. Ferrous iron (copper base cathode)
Curve 3. Ferric iron (copper base cathode)
Note: Only the points for Curve 2 are plotted.

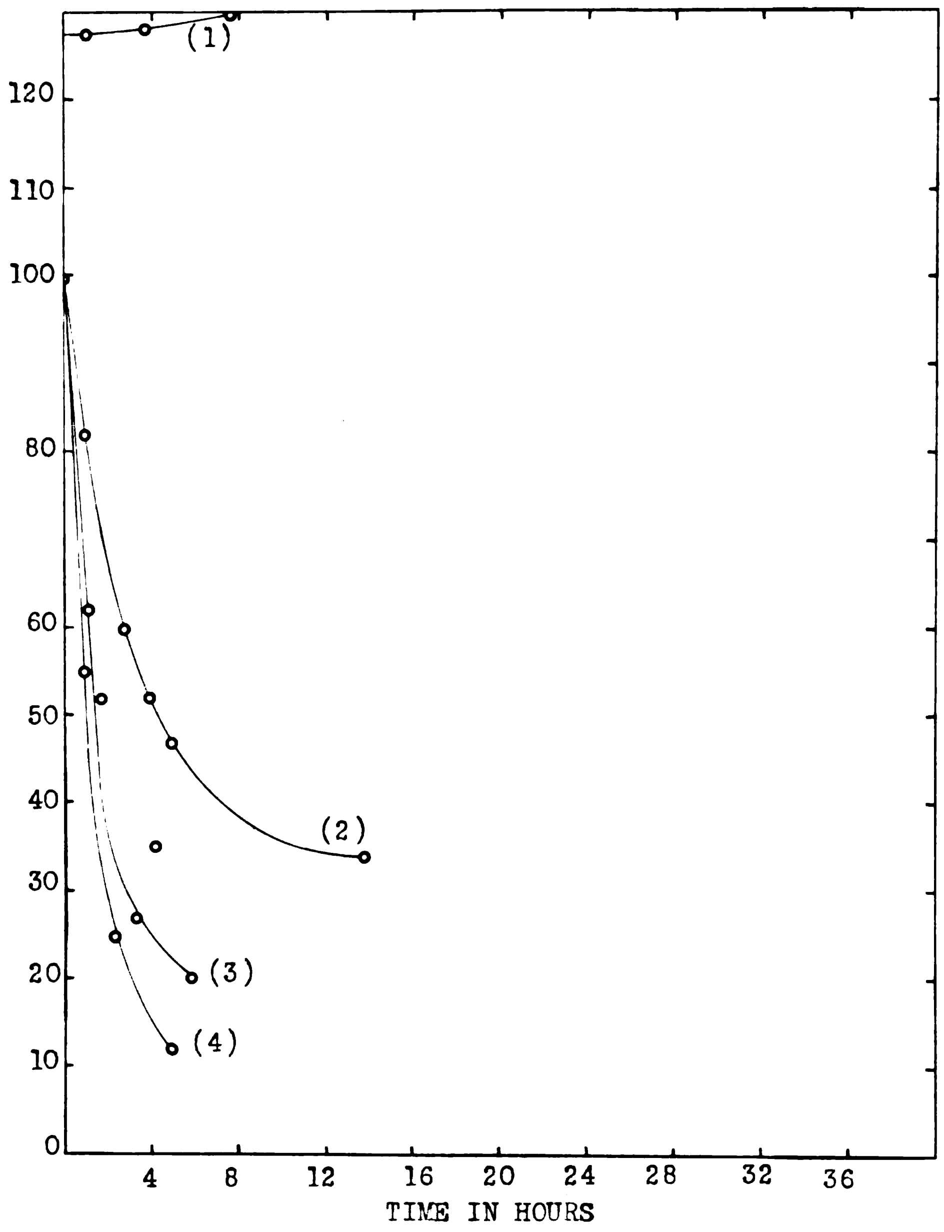


Fig. 10. Effect of Precipitation of the Hydroxide on the Electrolytic Removal of Iron from a 1% Nickel Cobalt Plating Solution. Curve 1. Precipitation Effect on a 2.1 pH bath. Curve 2. Optimum conditions of electrolytic removal from a 2.1 pH bath. Curve 3. Precipitation effect on 3.75 pH bath. Curve 4. Optimum conditions of electrolytic removal in a 3.75 pH bath.

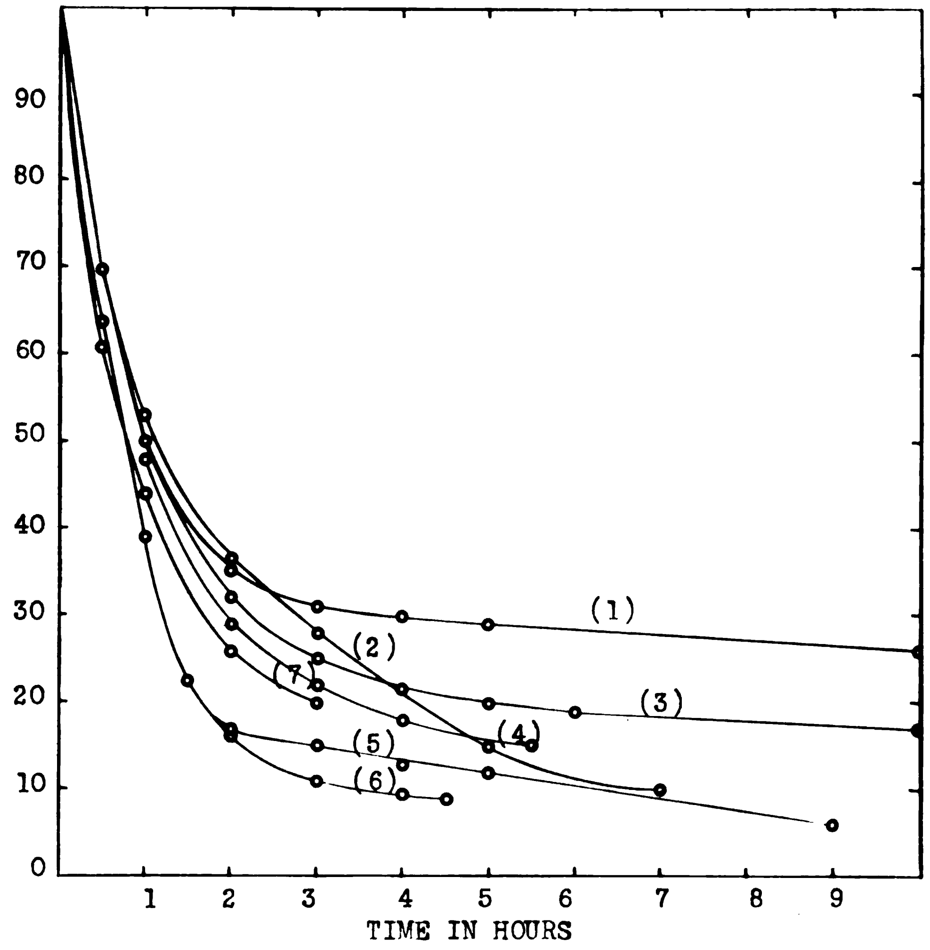


Fig. 11. Some of the Effects of Combined Precipitation and electrolysis in the Rate of Removal of Iron from a 3.75 pH 1% Nickel Cobalt Bath.

	Solution Agitation	Current Density	Temp. °C.	Cathode Indentation
Curve 1.	20 ft./min.	10 asf.	65	$\frac{1}{2}$ inch
Curve 2.	10 " "	10 "	80	" "
Curve 3.	20 " "	5 "	"	" "
Curve 4.	" " "	$7\frac{1}{2}$ "	"	" "
Curve 5.	" " "	10 "	"	3/4 "
Curve 6.	" " "	10 "	"	$\frac{1}{2}$ "
Curve 7.	Precipitation effect only.			

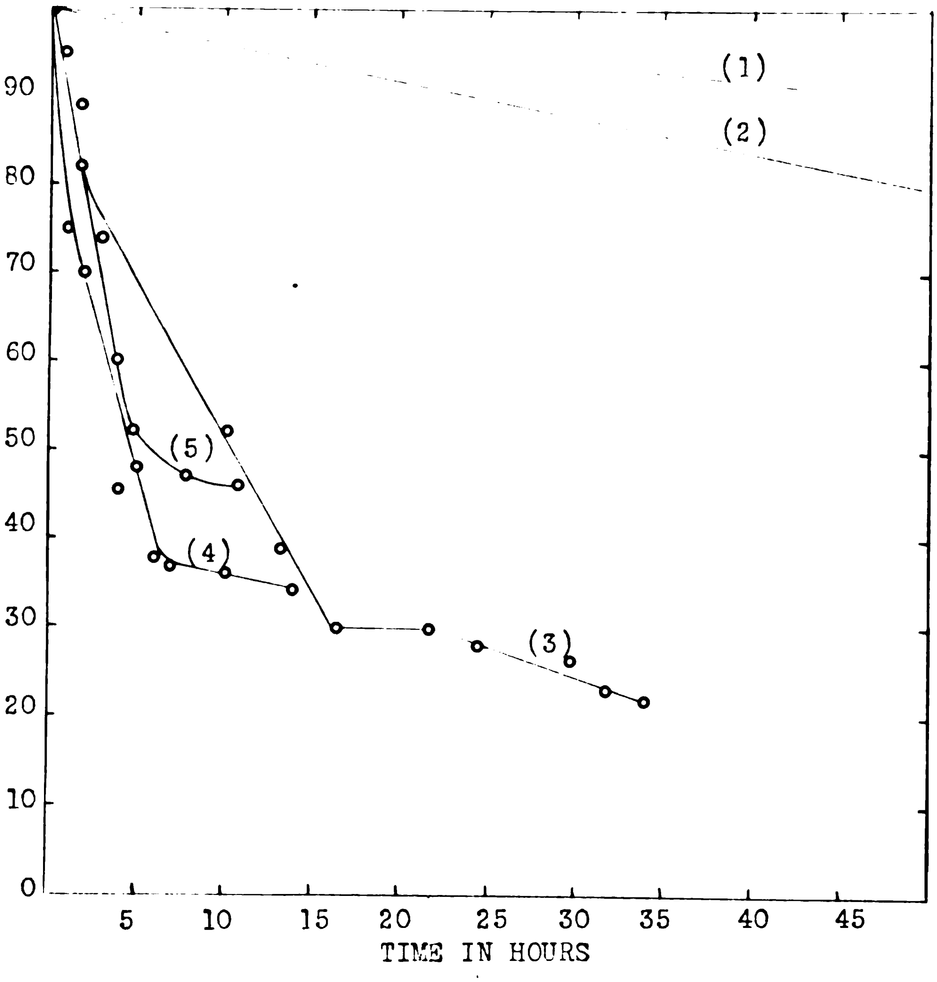


Fig. 12. Time Efficiency Against Amperes Per Square Foot Current Density in a 2.1 pH Nickel Cobalt Plating Solution.

Curve 1. 5 amps per ft.^{2} Curve 2. $7\frac{1}{2}$ amps per ft.^{2}
Curve 3. 10 amps per ft.^{2} (steel base cathode)
Curve 4. 10 amps per ft.^{2} (copper base cathode)
Curve 5. 15 amps per ft.^{2}

Discussion of Results- This discussion will present each of the variable conditions, temperature, cathode indentation, current density, and agitation, which were used in the electrolytic removal of iron from a 1% Nickel Cobalt plating bath and treat them in turn in two series, a 3.75 pH series, and a 2.1 pH series. The effect of chemical precipitation as it affects the electrolytic rate of removal of iron will then be discussed.

3.75 pH Series

Standard Conditions- 80°C. (175° F.), 1/2 inch cathode indentation, 10 amperes per square foot current density, 20 feet per minute solution agitation past the cathode, and ferric ion contamination at a pH of 3.75 (electrometric).

The temperature was varied from the standard 80°C. (175° F.) to 65° C. (150° F.) (Fig. 1) and very little difference in the effective rate of removal of the iron was noticed until a concentration of 40 to 50 milligrams per liter was reached. At this point the higher temperature (80° C.) continued to deplete the iron content to 8 milligrams per liter while the 65° C. temperature experiment began to level off near 30 milligrams per liter. This deviation was probably due to a combination of effects, namely, the increased precipitation of the hydroxide on increase in temperature and the enhanced electrolytic rate of removal. 80° C. (175° F.) was used subsequently as the best temperature.

The change in cathode indentation had no effect until the lower concentrations of iron were reached as shown in Fig. 2. The rate of removal of the iron was identical down to 25 milligrams per liter, at which point the 1/2 inch indentation cathode lowered the iron content to 10 milligrams per liter at 2000 ampere minutes per gallon while the 3/4 inch cathode needed 3400 ampere minutes per gallon to accomplish the same measure of purification. The 1/2 inch indentation was used for all subsequent cathodes.

The effect of a change in current density on the rate of removal of the iron was not as easily interpreted as the preceding variations. Five amperes per square foot current density removed the iron faster than 7.5 or 10 amperes per square foot until an iron concentration of 30 milligrams per liter was reached. (Fig. 3.) At this point 5 amperes per square foot rapidly leveled off. Seven and a half amperes per square foot current density removed the iron equally as fast as 5 amperes per square foot down to a concentration of 74 milligrams per liter. At this point it began to taper gently until at 30 milligrams per liter it began to level off but to a lesser extent than the 5 amperes per square foot curve. Ten amperes per square foot removed iron a little more slowly at the higher concentrations but continued to remove it down to 8 milligrams per liter at 2250 ampere minutes per gallon while 5 and 7.5 amperes per square foot were at 17.5 milligrams per liter and 14 milligrams per liter respectively. It would seem from these curves that the range of 25-35 milligrams per liter of iron is near a critical concentration above which iron is removed easily and below which more care in conditions of rate of removal must be exercised. This critical range is apparently a function of the chemical precipitation effect.

The effect of agitation on the rate of removal of iron was more regular than current density. Although the planned agitation variation called for series of 5, 10, 20, and 50 feet per minute solution flow past the cathode, later check measurements showed a 4, 5, 20, and 50 feet per minute series were actually accomplished. The 4 feet per minute of solution past the cathode removed the iron slowly at the higher concentrations (Fig. 4). However, it continued to remove iron in the concentrations below 15 milligrams per liter when higher agitation was much less effective. Five feet per minute removed the iron faster at higher concentrations than even 20 feet per minute but it began to lose effect at 55 milligrams per liter and followed the same rate as 4 feet per minute except that it had more tendency to level off under 10 milligrams per liter concentration of iron. Twenty feet per minute dropped the iron content fast and evenly to 25 milligrams per liter at which point it made a steeper leveling curve and is probably less effective in removing the remaining iron than the lower rates of agitation.

Precipitation affect

In order to insure that all removal was due to electrolysis, two runs were made, one on each pH bath, with heat and agitation, but no anodes, cathodes, or current used. Fig. 10, shows that there is no precipitation effect in the 2.1 pH series and that all of the removal is due to electrolysis. On the other hand, almost all of the removal of iron from the 3.75 pH bath is due to precipitation of the hydroxide and it is only after a concentration of 25 milligrams per liter has been reached that the electrolytic effect is noticed slightly. Precipitation will take place in the cold over a long period of time to the extent of about 38% of the original content in solutions with a pH range of 2.2 to 2.5 electrometric. This was determined by testing the original solutions used in making up the calibration curve for the iron analysis after a standing period of about 6 months.

2.1 pH Series

Standard Conditions- 80° C. (175° F.), 1/2 inch cathode indentation, 20 feet per minute agitation past the cathode, ferric ion, and a pH of 2.1.

After inspection of the results with the 3.75 pH series it was decided to accept the 80° C. (175° F.) temperature and the 1/2 inch cathode indentation as optimum conditions and not to vary these factors in the 2.1 pH 1% nickel cobalt solution experiments. Figure D, shows the effect of a circular steel cathode which had been previously plated with nickel but had cracked due to strains set up by plating only on the inside of the circle. This cathode was abandoned after determining by six more experiments that increased thickness of nickel deposited would not protect the steel and that it dissolved into the 2.1 pH solution as quickly as it was removed electrolytically. Ten and 7.5 amperes per square foot gave similar curves and 5 amperes per square foot actually increased the iron content. Even the straight corrugated cathode gave some iron into solution as shown in curves 2 and 3 of Figure 8. At 30 milligrams per liter on curve 2, the curve was level. However when a copper cathode was then introduced it lowered the iron content an additional 8 milligrams per liter. Therefore, when a check experiment was made (a cathode to be stripped and analyzed) a copper base cathode was used with the result that the rate of removal of iron (Fig. 8, curve 3) was increased in the higher concentration and leveled out at 35 milligrams per liter to a slope which indicated that it might reach 26.5 milligrams per liter in the same number of ampere minutes per gallon as the steel and copper cathodes of curve 2, Fig. 8 required.

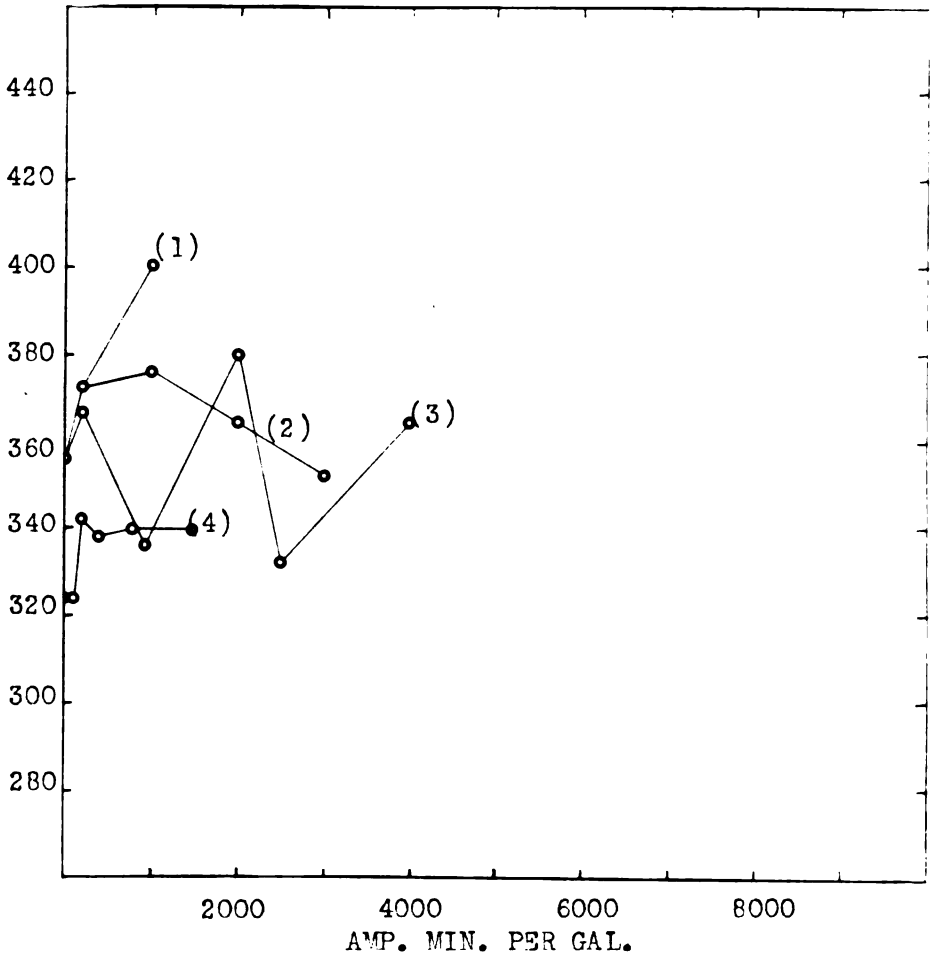


Fig. D. The Effect of a Circular Cathode on the Electrolytic rate of Removal of Iron from a 2.1 pH 1% Nickel Cobalt bath.
Curve 1. 5 amps per ft.^{2}. Curve 2. 10 amps per ft.^{2}.
Curve 3. 10 amps per ft.^{2}. Curve 4. $7\frac{1}{2}$ amps per ft.^{2}.

The effect of current density on the rate of removal of iron from a 2.1 pH 1% nickel cobalt plating solution is demonstrated in Fig. 5. Five amperes per square foot was very ineffective in removing iron since the curve leveled off at 65 milligrams per liter. Seven and a half amperes per square foot had about the same rate of removal of iron as 5 amperes per square foot but continued to remove iron down to a concentration of 35 milligrams per liter before leveling off. Ten amperes per square foot removed iron at a faster rate in the high concentrations; at about the same rate as 7.5 amperes per square foot for the portion of the curve from 80 milligrams per liter to 30 milligrams per liter; and than leveled until the copper cathode was introduced. Fifteen amperes per square foot had a faster rate of removal along the straight portion of the curve but leveled off at 45 milligrams per liter, well above the 10 amperes per square foot curve.

The effect of solution agitation on the rate of removal of iron from a 2.1 pH 1% nickel cobalt plating solution is shown in Fig. 6. Ten feet per minute past the cathode was very ineffective, leveling off at 80 milligrams per liter concentration of iron. Twenty feet per minute agitation was most effective, leveling off at 30 milligrams per liter. Fifty feet per minute caused a faster rate of removal in the higher concentrations, but below a concentration of 70 milligrams per liter it showed a slower rate of removal than 20 feet per minute solution agitation. A check experiment was made to verify this curve since theoretically more agitation should improve the rate of removal.

However, the check curve was identical except for the small portion of the curve from 400 ampere minutes per gallon to 1000 ampere minutes per gallon. This would seem to indicate a solution agitation optimum below 50 feet per minute and above 10 feet per minute.

The effect of a change in pH on the rate of removal of iron from a 1% nickel cobalt plating solution is evidenced in Fig. 7. The optimum rate of removal curves were used from each pH series. The 3.75 pH value is much more effective than a 2.1 pH since it removes the same amount of iron in about one sixth the number of ampere minutes per gallon down to a concentration of 30 milligrams per liter and levels off below 8 milligrams per liter as compared to 25-30 milligrams per liter leveling point of the 2.1 pH series. This is, of course, due to the large amount of chemical precipitation at the higher pH.

The effect of a flat cathode on the rate of removal of iron from a 2.1 pH solution is shown in Fig. 8. The flat cathode curve had no flat portions as had the corrugated cathodes version of rate of removal. It matched the optimum conditions until a concentration of about 70 milligrams of iron per liter was reached and gradually leveled out at 40 milligrams per liter at 6000 ampere minutes per gallon. This is a singular demonstration of the advantage of the corrugated cathode. Still it is a question whether the difference is entirely due to increased variation in current density or due partly to increased area of the cathode. The flat cathode had the least total area in

solution and removed iron most slowly. The 1/2 inch cathode indentation had 5 square inches more area and removed iron most rapidly in spite of the fact that the 3/4 inch cathode indentation had 22 square inches more area than the flat cathode. This would seem to indicate that it is not just increased area but also the corrugation effect which gives better conditions for removal of iron from a 1% nickel cobalt plating solution. In addition it might be stated that the 1/2 inch indentation seems to be near an optimum for cathode corrugation.

The ferrous ion was used (Fig. 9), to determine its effect on the rate of removal of iron from a 1% nickel cobalt plating solution. However, the analysis was very poor in this case in spite of checks and rechecks. It seems possible to assume however, that removal does not proceed much below 50 milligrams per liter and that the course of removal from 100 to 50 milligrams per liter is generally the same as for the ferric ion.

A rather peculiar effect was observed in the electrolysis of the 3.75 pH 1% nickel cobalt plating solution. (Fig. 11) The precipitation effect alone removed iron faster than some conditions of electrolysis. Curves #1, #2, #3, and #4 represent a lower temperature, slower agitation, and lower current density respectively than the optimum conditions. The lower temperature probably did not coagulate the precipitate as fast, and the failure of the lower current density to remove more iron may be explained by the equilibrium which will exist at the electrodes giving some ferrous ion at the cathode which cannot be precipitated. The decreased agitation (curve #2) should have had no effect on the precipitation behavior. However, it was not until after eight hours that this lower agitation exceeded the rate of removal of precipitation effect alone. Either the 3/4 inch or 1/2 inch cathode indentation at high temperature, agitation, and current density, removed iron faster than precipitation alone. After three hours, electrolytic removal by either of these cathodes had removed as much as the precipitation effect alone did in six hours.

All of the previous discussion has dealt with the differences in power efficiency of different sets of conditions. In order to show how time efficiency is affected with change in current density. The 2.1 pH series of current density curves are plotted with iron content against time in hours. (Fig. 12). This shows that in point of time, 10 amperes per square foot is again an optimum and that 7.5 and 5 amperes per square foot are not even feasable.

Conclusion- Certain conditions of electrolysis, namely, current density, agitation, and depth of cathode indentation, have an optimum, above and below which the rate of removal of iron from the 1% Nickel Cobalt solution will not be as rapid or effective. These optimum conditions (among those tested) are the following: current density 10 amperes per square foot; agitation 20 feet of solution past the cathode per minute; cathode indentation 1/2 inch. A temperature of 80° Centigrade was found superior to 65° Centigrade in the 3.75 pH bath.

Since the faster rate of removal obtained with higher temperature in the 3.75 pH bath was probably due to the increase of precipitation with temperature it is suggested that a lower temperature be tried in the 2.1 pH bath where there is no precipitation effect.

In dropping the concentration from 100 milligrams per liter to 35 milligrams per liter, a copper cathode will save 1500 ampere minutes per gallon over a steel base cathode when both have been operated at optimum conditions.

Future studies should include weighing of the cathode before and after each experiment to determine the nickel loss at different conditions. Optimum conditions have been established from 100 milligrams per liter down to 10 to 20 milligrams per liter. Further study on the lower limits of the 2.1 pH curves (20 mg./l. to 0 mg./l.) may be necessary if detrimental effects are still encountered at that concentration.

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