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THE SIMULTANEOUS ELECTRO-DEPOSITION OF COBALT AND NICKEL

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THE SIMULTANEOUS ELECTRO-DEPOSITION OF COBALT AND NICKEL

INTRODUCTORY

The object of this thesis is to determine and set forth a satisfactory method for the simultaneous electro-deposition of cobalt and nickel to form an alloy.

The results are qualitative, rather than quantitative, in their nature.

The experimental work may be grouped under three heads:-

1. Determination of a suitable electrolyte.
2. To control the distribution of current between the cobalt and nickel anodes. This is necessary if the bath is to remain of constant composition while in use.
3. To obtain deposits of varying composition by varying the relative amount of metals in the bath.

HISTORICAL

Nickel has long been used for the plating of various metallic objects. Articles may be electroplated for several reasons:-

1. For the prevention of corrosion.
2. For ornamental purposes.
3. For mechanical protection.

Nickel, by reason of its mechanical strength, chemical resistivity, and ability to take a high polish, has long been the metal most used in the field.

Its application, however, involves several undesirable features;

1. Low current densities are used, and the deposit builds up slowly.
2. For the best results, the bath must be kept hot.
3. On metals other than iron and steel, the object to be plated must first be flashed with copper.
4. Nickel has a tendency to peel, unless deposited under the most favorable conditions.

These disadvantages of nickel have finally lead to the investigation of other metals which might replace nickel, and in last few years cobalt has been given considerable attention.

The most notable work in this field has been accomplished by Dr.H.T.Kalmus, of Queens University, Ontario¹

In his general conclusions on cobalt plating he states:-

1. "Several cobalt solns. were found to be suitable for electro-plating with cobalt under the conditions of commercial practice.

Best among these were:-

Soln. IB:- $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ - - 200 gms./liter.

Soln.XIIIB :-

CoSO_4 - - - - 312 gms.

NaCl - - - 19.6 gms.

H_3BO_3 - - nearly to saturation.

Water - - - - 1000 cc.²

2. "Cobalt plates from these solns. on brass, iron, steel, copper, tin, German silver, lead, and Britannia metal articles. of different shapes and sizes, deposited under conditions identical with those met with in general nickel plating practice, are firm, adherent, hard and uniform. They may readily be buffed to a satisfactorily finished surface having a luster, which, although brilliantly white, possesses a slightly bluish cast".

4."Soln. I-B is capable of cobalt plating - - - -, at a speed at least four times that of the fastest satisfactory nickel solns".

5."Soln. XIII-B is capable of cobalt plating- - - -, at a speed at least fifteen times as great as the fastest satisfactory nickel solns".

11. "For many purposes, under the conditions of these rapid plating solutions, one fourth the weight of cobalt, as compared with nickel, is required to do the same protective work. Consequently, if nickel is worth 50¢ a lb. in the anode form, cobalt could be worth nearly \$2.00 a lb. in the same form, to be on the same basis, weight for weight of metal. In addition there are other advantages of cobalt in saving of labor, time, overhead, etc."

In the simultaneous electrodeposition of two metals, however, the situation becomes more complex. The conditions must be adopted to suit both metals. As stated by Blum & Hering² "the principles of alloy desposition are:-

1. Potentials in the solution concerned must be close,
2. Or, thru depolarization by one, the equilibrium discharge Potential of the other be altered so as to equal the first.

According to an anonymous article in the Brass World³ a solution of sulphates, 70 per cent Nickel and 30 per cent Cobalt and enough ammonium sulphate to make double sulphates was electrolyzed at two volts. A deposit of great hardness and white in color resulted. Difficulty in keeping the solution in working order will prevent its general use although it might be used in place of iron for coating electrotypes,- where great hardness is desired. It will not rust.

It is evident that, although cobalt plating has been worked out, the alloy plating has been left comparatively untouched.

The bluish color, which the pure cobalt deposit possesses, will work against its general acceptance in place of nickel. The buying public has been educated to expect a pure white plate, and will regard the bluish cast of the cobalt with suspicion.

If an alloy of cobalt and nickel were used, it might be possible to secure the combined advantages of both metals, and eliminate their disadvantages.

For instance, it might be possible to secure a plate, which, although rich in cobalt, possesses a pure white color. Moreover, alloys are often more resistant to corrosion and wear than are pure metals, and it might be possible to secure the same protective covering with a smaller amount of metal.

EXPERIMENTAL

The baths used consisted of (1) cobalt and nickel sulphates, (2) cobalt, nickel and ammonium sulphates, and (3) cobalt and nickel sulphates with various small amounts of addition agents. Chemically pure materials, because of their high cost, are not used in commercial plating. The cobalt and nickel sulphates used in these experiments, therefore, were of the commercial variety, partially purified by recrystallization. The best success was secured with a straight solution of the sulphates and addition agents, such as sodium or magnesium chlorides and potassium chlorate. The exact composition of the baths will be included in the data of the experiments.

The first attempts at plating cobalt and nickel were unsuccessful, but served as a guide in determining the difficulties to be overcome and the best means to use. Each problem and its solution will be treated separately.

DEPOSITION OF HYDROGEN:-

Attempts were made to plate from different mixtures of cobalt and nickel sulphates, but the deposits were invariably dark and discolored, - nor was this condition altered by changing the current density, concentrations of electrolyte, or temperature. No attempt was made to analyze these first deposits.

It was suspected that hydrogen, deposited simultaneously with the metals, caused the dark color, and this theory was supported by the fact that the addition of acid (hydrogen ions) to the electrolyte, greatly increased the blackening of the plate. This is in conformity with the results of other investigators.

In an article on "The Occlusion of Hydrogen by Cobalt and Other Metals", G. P. Baxter⁴ found that metallic cobalt absorbs up to forty eight volumes of hydrogen when heated and cooled in an atmosphere of that gas. Nickel absorbs ten to eleven volumes. He states that this absorption is slow at low temperatures, and also slow between four hundred and five hundred degrees Centigrade (temperature of reduction for the ores), but when cooled from the higher temperatures, the metals contain the given volumes of hydrogen. He concludes that the absorption is at a maximum somewhere between zero and five hundred degrees.

Raoult found, with less pure metal, that nickel will absorb one hundred and sixty five volumes of hydrogen⁵.

Curling up of the plate is often due to the simultaneous deposition of hydrogen with the metal⁶.

C. P. Madsen⁷ gives a method for avoiding the difficulty from hydrogen. In the deposition of cobalt, nickel, or alloys containing one or both, the cathode is periodically exposed to air for from one to two seconds, to allow the

hydrogen to escape. Exposure is made every one or two minutes. When the exposures are over six to sixteen seconds, laminated plates are produced.

THE USE OF DEPOLARIZERS FOR HYDROGEN:-

With the idea that the blackening effect of hydrogen could be reduced by the addition of an oxidizing agent, the following materials were tried:- (1) hydrogen peroxide, (2) potassium dichromate, and (3) potassium chlorate.

EXPERIMENT #1.

An electrolyte of cobalt and nickel sulphates, with hydrogen peroxide as an addition agent was tried. While not exhaustively studied, the addition of peroxide appeared to have no appreciable effect on the color of the plate. The dark color was unchanged. The use of hydrogen peroxide was abandoned.

EXPERIMENT #2.

In this experiment, potassium dichromate was added to a solution of cobalt and nickel sulphates in the hope of oxidizing the hydrogen as soon as it was discharged. The following electrolyte was chosen, because it approaches a saturated solution, which is the best condition for rapid plating of these metals.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 50 cc.
Nickel sulphate (300 grams per liter) - 50 cc.
Potassium dichromate - - - - - 1 gm.

Current density:- 2 amperes per square decimeter.

Voltage:- 0.8 volt.

Temperature:- 22°C.

Cathode:- Polished iron, one square centimeter.

The sulphates were dissolved in water and plating started before the dichromate was added. Within three minutes after the addition of the oxidizing agent, the plate had assumed a pure white color. In an hour, however, the plate became covered with a yellow-green paste. This product was not analyzed, but strongly resembled compounds of chromium. This corresponds to the thin film of chromium chromate which forms around the cathode during the manufacture of hypochlorites, when potassium dichromate is added to the electrolyte⁸.

The use of potassium chlorate, then, should be more successful since there is no reason for expecting the formation of a metallic compound similar to that formed with chromium.

EXPERIMENT #3.

The following conditions were observed:-

Electrolyte:- Cobalt sulphate (300 grams per liter) - 50 cc.

Nickel sulphate (300 grams per liter) - 50 cc.

Potassium chlorate:- - - - - 0.5 gram.

Current density:- 2 amperes per square decimeter.

Voltage:- 0.9 volt.

Cathode:- Polished iron, one square centimeter.

Distance between electrodes:- six centimeters.

Temperature:- 22°C.

At the end of an hour's run, there was a coal-black deposit one-eighth of an inch thick on the cathode. It resembled the oxide of cobalt. Dissolved in dilute hydrochloric acid, it gave a pink solution. Cobalt has been known, at low potentials, to plate as an oxide on the anode⁹. But its appearance as oxide on the cathode led to the conclusion that it must have been deposited first, and subsequently oxidized because of the chlorate present.

A lower concentration of depolarizer, then, should give the desired results. This was found to be the case in the following runs.

EXPERIMENT #4.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 60 cc.

Nickel sulphate (300 grams per liter) - 40 cc.

Potassium chlorate (10 grams per liter) - 3 cc.

Cathode:- Polished iron, one square centimeter.

Anodes:- Cobalt, five square centimeters;

Nickel, five square centimeters.

Distance between electrodes:- Six centimeters.

Temperature:- 22°C.

Log of run:-

Time	Amp.	Volt.	Remarks
10:20	.02	0.9	
10:50	.02	0.9	Plate dark and spotted. White rings showed location of bubbles. Added three cubic centimeters of potassium chlorate solution (ten grams per liter).
11:00	.52	1.0	Plate had turned pure white. There was no visible evolution of hydrogen.
11:20	.04	1.0	Plate dark in patches. Added four cubic centimeters of the oxidizing solution, - potassium chlorate, ten grams per liter.
11:30	.04	0.8	Plate improved, but still showed dark traces.

EXPERIMENT #5.

It is a well known fact that nickel anodes tend to become passive,- a condition that may be overcome by the addition to the electrolyte of a small amount of chloride. In this experiment one gram of sodium chloride has been added to the electrolyte, and the cathode has been more thoroughly cleaned. The other conditions were the same as in the preceding experiment.

Electrolyte:- Used electrolyte from experiment number four, adding one gram of sodium chloride.

Cathode:- Iron, one square centimeter; electrolytically cleaned in sodium hydroxide.

Other conditions remained constant.

Log of run:-

Time	Amp.	Volt.	Remarks
11:15	.04	0.7	
11:20	.03	0.6	The plate had started white in the center, dark on the edges,- therefor the current density was cut down.
11:30	.03	0.6	Plate still dark on edges. Added 3 cc. of potassium chlorate (ten grams per liter)
11:40	.03	0.6	Plate perfectly white, but blistered and peeled.

The tendency to peel was probably due to insufficient cleaning of the cathode, as it still showed traces of the oxide scale. The plate was of good color and hard. The

back surface of the electrode showed good plate with no tendency to peel. This would indicate too high a current density on the face.

EXPERIMENT #6.

This experiment was run under the same conditions as Experiment #5, except that a lower current density was used and still greater care was taken in cleaning the cathode.

Electrolyte:- used electrolyte remaining from experiment #5.

Cathode:- Iron,- ground,,polished, very thoroughly cleaned as cathode in sodium hydroxide, and washed.

Area, one square centimeter.

Other conditions:- Same as for experiment #5.

Log of run:-

Time	Amp.	Volt.	Remarks
1:35	.030	0.80	
2:00	.032	0.75	Plate still white.
5:20	.032	0.75	Plate very slightly discolored. Added 3 cc. of potassium chlorate.
5:35	.032	0.75	Plate good,- bright and velvety. Adherent, with no tendency to peel.

EXPERIMENT #7.

To determine the effect of varying the metal ion, the ratio of cobalt to nickel was reduced as shown below. As ammonium sulphate is often used in nickel baths, its effect was also tried in the mixed bath. Twenty six grams is the theoretic al amount of ammonium sulphate required to form the double sulphates. A total of thirty grams was added to insure complete conversion.

Electrolyte:-Cobalt sulphate (300 grams per liter) - 40 cc.
Nickel sulphate (300 grams per liter) - 60 cc.
Potassium chlorate (10 grams per liter) -3 cc.
Sodium chloride - - - - - 1 gm.

Cathode:- Iron, ground and polished. Electrolytic cleaner.
Area, one square centimeter.

Anodes:- Cobalt, five square centimeters;
Nickel, five square centimeters.

Distance between electrodes:-Six centimeters.

Temperature:- 22°C.

Log of run:-

Time	Amp.	Volt.	Remarks
10:25	.04	1.08	
10:55	.04	0.85	Plate very slightly dark. Added 3cc. of chlorate solution and 10 grams of ammonium sulphate.
11:10	.04	0.80	Plate considerably darker. Added 3cc. of the chlorate solution and 10 grams of ammonium sulphate.

11:35 .04 0.75 Plate streaked, uneven deposit, dark in color. Added 3cc. of the chlorate solution and 10 grams of ammonium sulphate.

11:40 .04 0.75 No improvement in plate.
Added 3 cc. of the chlorate solution.

11:45 .04 0.75 No visible change.

From this experiment, it would seem that the double sulphates do not give as satisfactory results for the combined plating of cobalt and nickel as do the straight sulphates.

Even if good plates were to be obtained from these ammonium compounds, it is doubtful if their use would be advisable because of the low solubility of the nickel complex. Gmelin-Kraut¹⁰ gives, for solubility in grams per liter at 23°C.:-

Cobalt sulphate - - - - - 380 grams.
Nickel sulphate - - - - - 379 grams.
Cobalt ammonium sulphate - - 171 grams.
Nickel ammonium sulphate - - 66 grams.

This decreased solubility would produce an electrolyte which has a much lower conductivity and which would be much slower in its plating.

EXPERIMENT #8.

This was run with the same electrolyte and under the same conditions as the preceding experiment.

Log of run:-

Time	Amp.	Volt.	Remarks
10:45	.03	0.92	
10:55	.03	0.85	Plate good. Added 3 cc. of potassium chlorate solution (10 grams per liter).
1:30	.03	0.85	Slightly dark. Added 3 cc. of potassium chlorate solution.
5:00	.03	0.70	Plate good,- bright and adherent.

The gradual drop in voltage may be due partly to polarization effects and partly to the fact that the iron cathode becomes covered over with an alloy of cobalt and nickel.

EXPERIMENT #9.

In this experiment the cobalt content of the electrolyte has been still further reduced.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 25 cc.

Nickel sulphate (300 grams per liter) - 75 cc.

Potassium chlorate (10 grams per liter) - 4 cc.

Sodium chloride - - - - 2 grams.

Other conditions still remained constant.

Log of run:-

Time	Amp.	Volt,	Remarks
2:40	.03	1.10	
2:50	.03	.98	Plate good but slightly dull.
3:10	.02	.70	Slightly dark. Added 3 cc. of potassium chlorate solution.
5:40	.02	.70	Plate good,- white, velvety, adherent.

Final weight of cathode:- 2.9425 grams.

Initial weight of cathode:- 2.8762 grams.

Weight of deposit:- - - .0663 grams.

Ampere-hours:- 0.063

Theoretical deposit, assuming 100 per cent nickel:- .0687 gms.

Theoretical deposit, assuming 100 per cent cobalt:- .0693 gms.

Assuming a 50 per cent alloy, this would, according to Faraday's law, give a current efficiency of $\frac{.0663}{.069}$, or 96 per cent.

The work thus far has been of a purely qualitative nature. It has shown, however, that it is possible to produce a deposit of cobalt and nickel alloy, and qualitative tests of the deposits showed the presence of both metals.

The next step was directed toward the control of the quantities of metals going into solution, and the quantities depositing. If the electrolyte is to give satisfactory service, its composition must remain very nearly constant; that is, the amount of nickel dissolving at the anode must equal the amount depositing at the cathode, and the amount of cobalt dissolving at the anode must equal the amount depositing at the cathode. This problem is best treated in two parts:-

1. Proper distribution of current between cobalt and nickel anodes.
2. The determination of the relationship between the ratio of cobalt and nickel in the electrolyte, and their ratio in the deposit.

The distribution of current at the anodes will be taken up first.

In the following set of experiments the current which flowed through the cobalt anodes and through the nickel anodes was recorded separately. The per cent of total current flowing through the cobalt anodes was calculated.

EXPERIMENT #10.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 50 cc.

Nickel sulphate (300 grams per liter) - 50 cc.

Cathode:- Iron.

Anodes:- Cobalt, 5 square centimeters,

Nickel, 5 square centimeters.

Distance between electrodes:- Six centimeters.

Temperature:- 22°C.

Data:-

Volt.	Amperes		total	% amps. thru Co.
	Ni	Co		
.2	-	.001	.001	-
.4	-	.002	.002	-
.6	-	.005	.005	-
.8	-	.010	.010	-
1.0	-	.017	.017	-
1.2	.001	.026	.027	96.0
1.6	.003	.042	.045-	93.4
2.0	.011	.056	.067	83.6
2.5	.023	.070	.093	75.3
3.0	.036	.085	.121	70.1

EXPERIMENT #11.

The electrolyte from experiment #10 was diluted with an equal volume of water, and one hundred cubic centimeters taken for the run. The other conditions remained constant.

Data:-

Volt.	Ni	Amperes Co	total	%amps. thru Co.
.2	-	.001	.001	-
.4	-	.004	.004	-
.6	-	.009	.009	-
.8	-	.014	.014	-
1.0	-	.021	.021	-
1.2	.001	.028	.029	96.5
1.6	.005	.042	.047	89.4
2.0	.009	.052	.061	85.2
2.5	.017	.066	.083	79.5
3.0	.027	.077	.104	74.0

EXPERIMENT #12.

In this experiment the cobalt content of the electrolyte has been increased, with the other conditions constant.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 75 cc.

Nickel sulphate (300 grams per liter) - 25 cc.

Data:-

Volt.	Amperes		total	% amps. thru Co.
	Ni	Co		
.2	-	.002	.002	-
.4	-	.008	.008	-
.6	-	.015	.015	-
.8	-	.024	.024	-
1.0	-	.037	.037	-
1.2	.0015	.0475	.049	97.0
1.6	.013	.065	.078	83.4
2.0	.027	.082	.109	75.0
2.5	.0455	.10.	.1465	69.0
3.0	.065	.125	.190	65.8

EXPERIMENT #13.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 25 cc.

Nickel sulphate (300 grams per liter) - 75 cc.

No other conditions were changed.

Data:-

Volt.	Amperes		total	% amps. thru Co.
	Ni	Co		
.2	-	.002	.002	-
.4	-	.006	.006	-
.6	-	.013	.013	-
.8	-	.023	.023	-
1.0	-	.035	.035	-
1.2	-	.044	.044	-
1.6	.005	.063	.068	92.8
2.0	.017	.080	.097	81.5
2.5	.033	.100	.133	74.5
3.0	.046	.130	.176	74.0

It is to be noted that with a lower ratio of cobalt in the electrolyte, more current flows through the cobalt anodes. This is in harmony with Wernst's solution theory.

EXPERIMENT # 14.

To determine the effect a change in the anode surfaces on the ratio of current passing through the individual anodes.

Anodes:- Cobalt, 5 square centimeters,

Nickel, 10 square centimeters.

Electrolyte and other conditions correspond to those in experiment #10.

Data:-

Volt.	Amperes		total	% amps. thru Co.
	Ni	Co		
.2	-	.002	.002	-
.4	-	.004	.004	-
.6	-	.008	.008	-
.8	-	.018	.018	-
1.0	.001	.028	.029	96.5
1.2	.004	.038	.042	90.5
1.6	.017	.055	.072	76.4
2.0	.031	.070	.101	69.1
2.5	.051	.090	.141	63.8
3.0	.070	.120	.190	64.1

EXPERIMENT #15.

To determine the effect of addition agents on the distribution of current.

Electrolyte:- Added one gram of sodium chloride to the electrolyte remaining from experiment #14.

Other conditions remained constant.

Data:-

Volt.	Amperes		total	% amps. thru Co.
	Ni	Co		
.2	-	.005	.005	-
.4	-	.012	.012	-
.6	-	.017	.017	-
.8	-	.024	.024	-
1.0	.001	.034	.035	97.2
1.2	.004	.045	.049	92.0
1.6	.021	.066	.087	76.0
2.0	.040	.088	.128	68.7
2.5	.060	.130	.190	68.5
3.0	.082	.160	.242	66.0

EXPERIMENT #16.

In this experiment, potassium chlorate was added to the electrolyte remaining from experiment #15. The electrolyte now contains all the addition agents necessary and is of the proper composition for producing the cobalt-nickel alloy.

Electrolyte:- Added 5 cc. of potassium chlorate solution (10 grams per liter) to the electrolyte remaining from experiment #15.

Other conditions remained constant.

Data:-

Volt.	Amperes		total	% amps. thru Co
	Ni	Co		
.2	-	.005	.005	-
.4	-	.013	.013	-
.6	-	.024	.024	-
.8	-	.037	.037	-
1.0	.008	.048	.056	85.7
1.2	.012	.060	.072	83.4
1.6	.030	.081	.111	73.0
2.0	.041	.110	.151	73.0
2.5	.066	.135	.201	67.0
3.0	.094	.165	.259	63.5

EXPERIMENT #17.

To determine the effect of still further reducing the ratio between the surfaces of cobalt and nickel in the anodes, the following test was made.

Electrolyte:- Used electrolyte remaining from experiment #16.

Anodes:- Cobalt, 2.5 square centimeters,

Nickel, 10 square centimeters.

Other conditions constant.

Data:-

Volt.	Amperes		total	% amp. Co.
	Ni	Co		
.8	-	.028	.028	-
1.0	.006	.038	.044	86.3
1.2	.018	.046	.064	71.8
1.4	.035	.056	.091	61.5
1.6	.050	.064	.114	56.1
1.8	.064	.071	.135	52.5
2.0	.080	.079	.159	49.6
2.5	.130	.089	.219	40.6
3.0	.170	.115	.285	40.4

A survey of the above data points to the following conclusions:-

1. The principal method of securing proper distribution of current between the cobalt and nickel anodes must be through the ratio of their surfaces (see experiments # 10-14-16-17). The ratio of surfaces must be adjusted for each experiment so as to be in accord with the variable conditions.
2. At the usual plating voltages, the ratio of current entering through the nickel anodes will increase with increased voltage. The range is large enough to be of some value in controlling the ratio between the two entering currents, but cannot be used through any great range.
3. The addition agents (sodium chloride and potassium chlorate) have some effect on the distribution of current at the anodes but not sufficient to be of value.
 - A. Sodium chloride increases the conductivity of the electrolyte, but has only slight effect on the percent of current passing through the different anodes.
 - B. The small concentration of potassium chlorate used acts with approximately the same result. Its effect is more noticeable at low voltages.

4. The ratio of metal ion in the electrolyte will have an effect on the distribution of current. This, however, is of little importance, since the ratio of the metals in the deposit determines the ratio of metal ions in the electrolyte.

The next consideration is the relationship between the ratio of metals in the bath, and their ratio in the deposit. G. Bruni and M. Amaderi published an article on the "Formation of Metallic Alloys by Electrolysis"¹¹. The authors experimented with "copper-nickel, iron-nickel, iron-cobalt, nickel-cobalt, and mixtures of the two metals in each case were obtained by electrolysis. The composition of the deposit varies as the ratio of the metals in solution. The ratio is practically equal to that in the deposits when the current density and potential at the electrodes are high. When the current density and tension are diminished, the deposits contain that metal in larger proportion which is lower in the electromotive series. Ammonium salts and ammonia tend to increase the deposit of nickel in the copper-nickel alloy. The per cent of Nickel diminishes on using a rotating cathode. Analogous results are obtained with copper-cobalt. The pair iron-nickel shows more complex phenomena with weak current density (.05 amperes per

square decimeter). Solutions containing 40-75 per cent iron give deposits of constant composition, with about 52 per cent iron, while for solutions of other composition, the deposits vary in composition with variation in composition of the solution. Cobalt-iron mixtures behave in a similar manner. Solutions containing 33.3-50 per cent iron give deposits of a constant composition".

No definite mention is made of the nickel-cobalt mixture.

EXPERIMENT #18.

In this experiment, magnesium chloride was used in place of sodium chloride, since it gives better corrosion of the anodes.

Electrolyte:-Cobalt sulphate (300 grams per liter)- 100 cc.
Nickel sulphate (300 grams per liter)- 100 cc.
Potassium chlorate (10 grams per liter)-10cc.
Magnesium chloride - 2 grams.

Anodes:- Cobalt, 0.5 square centimeter;

Nickel, 15 square centimeters.

Cathode:- Iron eight square centimeters.

Temperature:- 22°C.

Log of run:-

Time	Amperes		total	E.M.F. Volt.
	Ni	Co		
2:30	.04	.04	.08	2.0
3:20	.03	.03	.06	1.5
4:30	.04	.04	.08	1.5
4:35	.04	.04	.08	1.7
4:40	.04	.04	.08	1.5
5:30	.06	.06	.12	1.9
5:40	.04	.04	.08	1.5

Plate good,- white, velvety, hard and adherent.

Analysis showed 12 per cent nickel.

EXPERIMENT #19.

In this experiment the ratio of cobalt to nickel has been decreased, so as to decrease the percentage of cobalt in the deposit.

Electrolyte:-Cobalt sulphate (300 grams per liter) - 50 cc.

Nickel sulphate (300 grams per liter) - 150 cc.

Potassium chlorate (10 grams per liter) - 10 cc.

Magnesium chloride - - - - - 2 gm.

Anodes:- Cobalt, 0.5 square centimeters,

Nickel, 15.0 square centimeters.

Cathode:- Iron, eight square centimeters.

Temperature:- 22°C.

Log of run:-

Time	Volt.	Amperes		total
		Ni	Co	
3:30	2.1	.06	.06	.12
3:40	2.0	.04	.04	.08
4:00	2.0	.06	.06.	.12
4:25	2.0	.064	.064	.128
4:30	2.0	.064	.064	.128

Potassium chlorate solution was added, when necessary to prevent discoloration of the deposit.

Final plate was of good color and adherent.

Analysis showed 37 per cent nickel.

EXPERIMENT #20.

In this experiment the ratio of cobalt to nickel has been still further reduced.

Electrolyte:- Cobalt sulphate (300 grams per liter) - 20 cc.

Nickel sulphate (300 grams per liter) - 180 cc.

Potassium chlorate (10 grams per liter) - 10 cc.

Magnesium chloride - - - - 2 grams.

Other conditions remained the same.

Log of run:-

Time	Volt.	Amperes		
		Ni	Co	total
9:30	1.8	.06	.06	.12
10:00	1.7	.06	.06	.12
11:30	1.6	.06	.06	.12

The first deposit showed a slight discoloration, which soon disappeared. Final plate was good.

Analysis showed 71.2 per cent nickel.

EXPERIMENT #21.

With higher current densities, the ratio of metals in the deposit should more nearly approach their ratio in the electrolyte.

Electrolyte:- Used electrolyte remaining from experiment #20.

Anodes:- Cobalt, 0.4 square centimeter,

Nickel, 20 square centimeters.

Cathode:- Iron, eight square centimeters.

Temperature:- 22°C.

Log of run:-

Time	Volt.	Amperes		total
		Ni	Co	
2:00	2.2	.13	.04	.17
2:30	2.1	.12	.04	.16
3:10	2.2	.14	.04	.18
3:55	2.0	.12	.04	.16

Plate was white, hard and adherent, with its nickel content somewhat increased.

Analysis showed 76.1 per cent nickel.

FINAL CONCLUSIONS

From the above experiments we may draw the following conclusions:-

1. It is possible to produce a deposit containing both nickel and cobalt, which is hard and adherent. A slightly bluish cast (much less than is the case with pure cobalt) is noticeable when the plate is first made. This tends to disappear after several months.
2. It is possible, by variation of the impressed voltage and of the relative surfaces of cobalt and nickel in the anode, to control the amount of current entering through each anode, This is necessary if the composition of the bath is to remain constant.
3. It is possible, by varying the ratio of metals in solution, to produce good plates of different composition, varying from twelve to seventy six per cent nickel.
4. The most suitable electrolyte is a solution of the sulphates of cobalt and nickel, totaling 300 grams per liter, the ratio depending on the ratio desired in the deposit. Ten to fifteen grams per liter of magnesium chloride aids in maintaining a bath of uniform concentration, since better corrosion of the nickel anodes is secured.
5. Simultaneous deposition of hydrogen may be avoided by adding a solution of potassium chlorate. The electrolyte should receive about 5 per cent by volume, of a solution containing ten grams per liter.

6. Current density must not exceed 3-4 amperes per square decimeter.

7. The impressed voltage should be 1.25 or above, as the nickel anodes do not function much below this point.

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