ELECTRODEPOSITION

of

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NICKEL-COBALT ALLOYS

A Preliminary Report

THE *Bendix*
CORPORATION
KANSAS CITY DIVISION

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ELECTRODEPOSITION OF NICKEL-COBALT ALLOY:

Operating Parameters and Physical Properties of the Deposits

A PRELIMINARY REPORT

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I. ABSTRACT

Nickel-Cobalt alloys deposited from a sulfamate bath are described with respect to solution operating parameters and the physical properties of the deposits obtained. The effects of the solution metal ratios, anode characteristics, bath temperature, boric acid contents and applied current densities on the deposit compositions obtained are discussed. Physical properties (tensile strength, yield strength, elongation, hardness and grain structures) of the alloy deposits are correlated with composition and heat treatments up to 1150° F. Also, the properties of pure nickel and pure cobalt deposits produced from the basic sulfamate solution along with nickel deposits produced from solutions containing selected additives are discussed. Testing procedures, equipment and analytical techniques utilized for bath control and deposit testing are described.

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III. INTRODUCTION

The electroplating and electroforming of nickel, cobalt, and nickel-cobalt alloys have been investigated and reported for various systems. The systems which have been investigated include the: chloride, sulfate, sulfamate, pyrophosphate, fluoboric, various organic base and combination systems.⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾⁽⁷⁾ The major amount of data that has been presented in the literature on electroforming characteristics, properties and techniques have been primarily concerned with the deposition of pure nickel.⁽⁸⁾⁽⁹⁾⁽¹⁰⁾⁽¹¹⁾ Relatively few references were found in the literature regarding cobalt systems and nickel-cobalt alloy systems, and the references have pertained mainly to electroplating applications, with major emphasis on the physical and chemical characteristics of the plating solutions and the resultant deposits.⁽³⁾⁽¹²⁾⁽¹³⁾

The utilization of a sulfamate system for both electroplating and electroforming applications, of several metals, was pioneered by Piontelli, Cambri and Giulotto, and first applied as a commercial process by Barrett.⁽¹⁴⁾ Venkatachalm and Rama Char,⁽¹⁵⁾ Tsu and Fritsch,⁽¹⁶⁾ Eisler⁽¹⁷⁾ and Barrett have investigated the nickel, cobalt, and nickel-cobalt sulfamate systems and reported on solution operating parameters, deposit characteristics and the effects of various solution additives. Other investigators; Sample and Knapp,⁽¹⁸⁾ Diggin,⁽¹⁹⁾ Fanner and Hammond,⁽²⁰⁾ Asher and Harding⁽²¹⁾ have investigated the nickel sulfamate system and determined various physical and chemical properties of the electrodeposits.

Design and economic considerations have resulted in wide application of electroforming principles using nickel or nickel alloy systems.⁽²²⁾⁽²³⁾⁽²⁴⁾ The physical property data covering the complete composition range for nickel-cobalt alloys are not available for any of the systems reported; and, as might be expected, there is relatively little correlation between data for similar compositions obtained from the different systems.

This study was undertaken to provide information over the complete nickel-cobalt alloy compositions as obtained from a single system so that the data could be readily utilized in electroforming design. The sulfamate base system was selected because (1) it has proven to be the best electroform system available for nickel and (2) cobalt is readily compatible.

IV. EXPERIMENTAL DESIGN

The investigations performed on the nickel-cobalt alloy plating system were conducted in three phases. The first phase consisted of specific tests conducted on a laboratory scale so that the basic operating parameters of the alloy plating system could be determined. The second and third phases comprised the plating and testing of specimens for the determination of the physical properties of the deposits. The ultimate tensile strength, yield strength, hardness, elongation and grain structures of these deposits were determined after various degrees of heat treatment. The second phase was directed toward nickel-cobalt alloy deposits containing from 0% to 100% nickel obtained from the sulfamate system using bromide as the anode corroding agent. The third phase was directed toward determining the effects various solution additives impart to the pure metal and alloy deposits.

A. Preliminary Investigations

The operating parameters of the basic alloy plating solutions were obtained using one (1) liter solutions, accurately formulated from the basic materials. The tests were run in a one (1) liter graduated beaker with heat and agitation supplied by a magnetic stirring hot plate. The agitation was supplied by Teflon coated spin bars and temperatures were measured with a 0 - 220° F. glass thermometer. Plating tests were conducted using pure platinum discs (1 inch diameter by 0.030 inches thick) as cathodes suspended in the solution with platinum wire.

Two to four test specimens, weighing approximately 0.4 gram each were plated from each set of solution conditions. A maximum of approximately 1.6 grams was deposited from each one (1) liter solution before any metal additions were made and no bath adjustments

were made during the plating of a test specimen. The deposits obtained were dissolved with 30% (by vol.) nitric acid at 60 - 71° C. (140 - 160° F.), and were analysed by an x-ray fluorescence method. (The procedure is described in Appendix Section 2.)

The nickel-cobalt bath formulations used for the preliminary determinations are shown in Table 1.

B. Physical Property Determinations

The physical properties of the pure nickel and cobalt metals and their alloys were determined from tensile specimens produced in 28 liter (7.5 gal.), 68 liter (18 gal.) or 76 liter (20 gal.) plating solutions. The equipment and techniques used for preparing the specimens are discussed in the following sections.

1. Plating Set-Up Type 1 - Split Current Type--Figure 1. The solution metal balance was maintained by using nickel and cobalt anodes and controlled by a split current system.

Item #1 18" x 20" x 20" PVC coated stainless steel tank (76 liters) equipped with two (2) 1000 watt quartz heaters, heater controller, agitator, nickel and cobalt anodes and a specially designed lucite tank cover. (Tests using the split anode system were also conducted in 18" diameter by 20" high Pyrex tanks fixtured in the same manner.)

Item #2 The current splitting device utilized to proportion the proper amount of current to each anode (Circuit Diagram--Figure 32, Appendix Section 3).

Item #3 Filter Unit--Sethco Model APHI-10V Filter, equipped with a one (1) micron, dynel filter tube, Sethco Special "C".

TABLE 1.

SOLUTION COMPOSITION FOR PRELIMINARY TESTS

COMPONENT	CONCENTRATION
Ni + Co (a)	78.8 gm/l
Ni/Co Ratio	0.11 - 100
H ₃ BO ₃	30 - 45 gm/l
NiBr ₂	14 gm/l
Wetting Agent (b)	30 dynes/cm ²
CONDITIONS	
Temperature	38 - 60° C. (100 - 140° F.)
Current Density	2 - 5 amp/dm ² (20 - 50 ASF)
Anode/Cathode Ratio	3:1
Anodes (c)	Pure Ni or Pure Co
pH (electrometric) (d)	4.0

(a) Added to solution as sulfamates.

(b) Sodium lauryl sulfate.

(c) Not bagged.

(d) Adjusted with sulfamic acid.

FIGURE 1. PLATING SET-UP TYPE 1. - SPLIT CURRENT TYPE

Item #4 Current-Time Integrator--Weston Model 1473 Ampere

Minute Meter used to monitor all specimen plating cycles.

Accuracy of unit $\pm 0.5\%$ at any input.

Item #5 Electro Products Model No. D-612T, 0 - 10 amps, 0 - 20

volts, filtered power supply equipped with a 0 - 10

amp expanded scale meter. A 25 mv 10 amp shunt (accuracy $\pm 0.05\%$) was installed and used as the integrator signal source.

2. Plating Set-Up Type 2 - Metering Type--Figure 2. The solution metal balance was maintained by nickel anodes and metered cobalt additions.

Item #1 16" diameter by 12" Pyrex tank (~ 28 liter) equipped with one (1) 1000 watt quartz heater and controller, agitator, glass thermometer, two (2) pure nickel anodes, specially designed tank cover, and variable speed specimen plater (Figure 3). (Tests using the metering system were also conducted in 18" diameter by 20" high Pyrex tanks fixtured in the same manner.)

Item #2 Metering Pump--Beckman Model No. 746, 0 - 5 ml/min solution metering pump. This unit was used to add amounts of cobalt sulfamate and wetting agent into the plating bath at predetermined rates.

Item #3 Variable Speed Motor and Controller--Bodine Model NSH-12R variable speed motor and control unit used to rotate specimen holder at 7 RPM during test periods.

Item #4 Filter Unit--Sethco Model AVAI-3TCZ filter equipped with a 3 micron, dynel filter tube.

FIGURE 2. PLATING SET-UP TYPE 2. - METERING TYPE

Item #5 Current Time Integrator--(See Section 1, Item #4.)

Item #6 Rectifier--(See Section 1, Item #5.)

3. Plating Set-Up Type 3 - Conventional Type--This equipment type was used to obtain the pure nickel deposits produced during the investigation and is similar to Type 1 (Split Current Type) except that the current splitting device was not incorporated.
4. Specimen Plater--Figure 3 shows the specially designed tensile specimen plater used to produce a family of 5 specimens simultaneously. This approach to specimen plating was utilized because:
 - a. Five specimens were required to determine the physical properties of the deposits at the heat treatments selected.
 - b. Uniformity of deposit thickness was desired so that side effects in the physical properties caused by thickness variations (i.e., current density variations) would be minimized.
 - c. To obtain deposits which were produced under a controlled current density gradient which would more closely approximate average electroplating or electroforming applications.

Electrical contact is made to each test panel by two button contacts imbedded in the Lucite supporting frame behind the panels. Each contact was placed two inches from the end and on the centerline of the panels. Masking and clamping was accomplished by beveled (45°) Lucite strips held in place by nylon screws. Also shown, is the electrical contact mechanism used to maintain electrical connection to the rotating specimen holder. The unit consists of a spring loaded copper brush, holding assembly and a brass slip ring. The slip ring is isolated, electrically from the motor drive shaft by a bakelite coupling. A mixture of petroleum jelly and graphite powder was used as an electrically conductive lubricant for the assembly.

FIGURE 3. SPECIMEN PLATER AND ELECTRICAL CONTACT ASSEMBLY

5. Physical Test Specimens—Figure 4 shows the physical appearance of the specimens at different times during fabrication and Figure 5 shows the finish tolerances used in the final tensile specimen preparation. All physical test specimens were prepared using the following process (except where specifically noted).
- a. 1" x 8" x 0.030" panels were cut from 2024 aluminum sheet.
(Figure 4-a)
 - b. The panels were cleaned, zincated, copper flashed (cyanide copper) and then gold plated to 0.00015" (cyanide gold).
(Figure 4-b)
 - c. 5 panels were placed in the specimen plater (Figure 3), plated at a current density of 3 amp/dm² (30 ASF) for 3500 amp-minutes and then removed from the fixture. (Figure 4-c)
 - d. The gold plate and copper flash were stripped from the back of the panels with Aurostrip 407^{/1}.
 - e. The aluminum panels were removed by dissolving with a sodium hydroxide solution (~60 gm/l) at 150 - 170° F. (Figure 4-d)
 - f. The copper flash and gold plate were stripped from the back of the specimen with Aurostrip 407.
 - g. The specimens were heat treated to the specified temperatures as described in Section IV. C. and then machined to tensile test specifications. (Figure 4-e and Figure 5.)
6. Plating Bath Formulations--The operating parameters of the various sulfamate solutions utilized for the investigative work are presented in Table 2.

/1 Aurostrip 407. MacDermid Inc., Waterbury, Conn.

FIGURE 4. TEST SPECIMEN PROCESSING APPEARANCE

1 All exterior edges of the tensile specimen must be polished to eliminate all cutting notches by the following process or one which will give an equivalent finish. (1) 240 grit paper then (2) 400 grit paper then (3) 600 grit paper then (4) finish with a very fine emery paper.

FIGURE 5. Tensile Specimen Dimensions (ASTM - F2 Tensile Bar Method 211.1)

TABLE 2.

PLATING BATH FORMULATIONS (a)

Bath Type

Operating Conditions

A.	Nickel Sulfamate (as Nickel) Boric Acid Magnesium Chloride pH (electrometric) Surface Tension (b)(f) Temperature Anodes	72.0 - 85.0 gm/l 34.0 - 44.0 gm/l 3 - 4.4 gm/l 3.5 - 4.0 30 - 32 dynes/cm ² 120° F. (49° C.) Rolled Depolarized Nickel
B.	Nickel Sulfamate (as Nickel) Boric Acid Nickel Bromide pH (electrometric) Surface Tension (b) Temperature Anodes	81 - 81.7 gm/l 29.4 - 31.5 gm/l 13.3 - 14.2 gm/l 4.0 - 4.1 30.4 - 31.3 dynes/cm ² 120° F. (49° C.) Pure Nickel
C.	Cobalt Sulfamate (as Cobalt) Boric Acid Cobalt Bromide pH (electrometric) Surface Tension (b) Temperature Anodes	78 - 79.5 gm/l 30 - 30.2 gm/l 14.2 gm/l 3.95 - 4.0 28.5 - 30 dynes/cm ² 120° F. (49° C.) Pure Cobalt
D.	Nickel Sulfamate (as Nickel) Boric Acid Magnesium Chloride N.T.S.A. (naphthalene Trisulfonic acid, sodium salt) pH (electrometric) Surface Tension (b)(f) Temperature Anodes	75 - 80 gm/l 29 - 31 gm/l 4.7 - 5.5 gm/l 8 - 8.2 gm/l 4.0 - 4.3 30 - 32 dynes/cm ² 120° F. (49° C.) Rolled Depolarized Nickel
E.	Nickel Sulfamate (as Nickel) Boric Acid Nickel Bromide N.T.S.A. (naphthalene trisulfonic acid, sodium salt) pH (electrometric) Surface Tension (b)(f) Temperature Anodes	74.5 - 76.8 gm/l 28.4 - 30.1 gm/l 7.9 - 8.6 gm/l 7.8 - 8.3 gm/l 4.0 - 4.3 30 - 32 dynes/cm ² 120° F. (49° C.) Rolled Depolarized Nickel

F.	Nickel Sulfamate (as Nickel)	75 - 77.4 gm/l
	Boric Acid	28.4 - 30.1 gm/l
	Magnesium Chloride	4.3 - 4.9 gm/l
	N.T.S.A. (naphthalene trisulfonic acid, sodium salt)	8.6 - 8.8 gm/l
	Perflow (c)	~1.0 gm/l
	pH (electrometric)	3.95 - 4.2
	Surface Tension (d)(f)	30 - 32 dynes/cm ²
	Temperature	120° F. (49° C.)
	Anodes	Rolled Depolarized Nickel
G.	Total Metal (Nickel + Cobalt)	82 - 94 gm/l
	Nickel/Cobalt Ratio (e)	See Figure 7
	Boric Acid	29.6 - 31.5 gm/l
	Nickel Bromide (or)	12.4 - 15.2 gm/l
	Cobalt Bromide	13.6 - 14.2 gm/l
	pH (electrometric)	3.8 - 4.2
	Surface Tension (b)	26.4 - 31.1 dynes/cm ²
	Temperature	120° F. (49° C.)
	Anodes	Pure Nickel and/or Pure Cobalt

- (a) Typical analysis of components, Table 3.
- (b) The surface tension was maintained with sodium lauryl sulfate.
- (c) A Leveling Agent manufactured by the Harshaw Chemical Co., Cleveland, Ohio.
- (d) The surface tension was maintained with XXX-D. Manufactured by the Harshaw Chemical Company, Cleveland, Ohio.
- (e) Nickel and Cobalt were added as the sulfamates.
- (f) Conversion from 4 inch diameter ring determination to cgs system.

C. Testing Procedures and Equipment

The effects of heat treatment on the electrodeposits were obtained at 450°, 650°, 850° and 1150° F. using four specimens of each family of five. The fifth specimen was used to obtain the as plated properties of electrodeposits. The equipment, procedures, techniques, and materials used to evaluate the test specimens are described in the following sections.

1. Heat Treatment--Each specimen from a family of five parts, plated simultaneously, was heat treated by the following procedure in an Ipsen Vacuum Furnace Model No. VFC-L-30.
 - a. Place the specimens in the holder (Figure 6), put into furnace and reduce pressure to 0.1 micron.
 - b. Heat specimen up to specified temperature and maintain at specified temperature for 10 minutes.
 - c. Argon quench and remove from furnace.
2. Hardness Measurements--Hardness measurements were made on a Wilson Tukon Microhardness Tester using a 500 gram load. All hardnesses were obtained from the tensile specimens in the neck area adjacent to the fracture, after tensile testing, and are reported on the Knoop scale.
3. Photomicrographs--Sections of the tensile specimen from the neck area, after tensile testing, were mounted and polished using standard metallographic procedures. The polished specimens were microetched with a solution of 50% (by vol.) concentrated nitric acid and 50% (by vol.) concentrated acetic acid using contact times of 5 - 10 seconds. The photomicrographs were made with a Polaroid camera using a Bausch and Lomb Research Metallograph.

4. Physical Properties--The ultimate strength, yield strength, elongation and modulus of elasticity were determined from the tensile test specimens using a Baldwin Universal Testing Machine and a 2 inch gage length Baldwin Extensimeter. The determinations were made with a crosshead speed of 0.050 inches per minute. The yield strengths were determined by the 0.2% offset method and the modulus taken as the initial tangent to the stress-strain curve. The modulus of elasticity data is available but not presented in this report.
5. Materials and Reagents--The materials used to formulate the various solutions utilized for the experimental work were of the highest chemical purity available. The nickel and cobalt sulfamates used for solution make-up were obtained from commercial suppliers and were carbon treated prior to use. Typical analyses of the materials and reagents utilized are presented in Table 3.

FIGURE 6. HEAT TREATMENT SPECIMEN HOLDER

TABLE 3.

SPECTROGRAPHIC ANALYSIS OF MATERIAL AND REAGENTS (a)

Element	Nickel Bromide Solution	Nickel Sulfamate Solution	Cobalt Sulfamate Solution	Nickel Rod (Anode)	Cobalt Rod (Anode)	Cobalt Bromide Crystals	Boric Acid	Sodium Lauryl Sulfate
Cobalt (%)	0.01	0.01	M. C.	0.01	M. C.	M. C.	<0.001	0.001
Calcium (%)	0.1	0.1	0.1	0.001	0.001	0.001	0.001	0.001
Boron (%)	0.001	0.1	<0.001	<0.001	<0.001	<0.001	M. C.	<0.001
Silicon (%)	0.005	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Manganese (%)	0.0001	0.003	0.003	<0.001	<0.001	<0.001	<0.001	<0.001
Magnesium (%)	0.01	0.01	0.01	0.001	<0.001	<0.001	0.01	0.0001
Lead (%)	<0.001	<0.001	0.01	<0.001	<0.001	<0.001	<0.001	<0.001
Tin (%)	<0.001	<0.001	0.005	<0.001	<0.001	<0.001	<0.001	<0.001
Copper (%)	0.001	0.005	0.01	0.0001	0.0001	<0.0001	<0.0001	0.0001
Zinc (%)	0.01	0.01	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sodium (%)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	M. C.
Silver (%)	<0.0001	0.0001	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Aluminum (%)	0.01	0.01	0.001	0.01	0.001	0.001	0.001	0.001
Nickel (%)	M. C.	M. C.	0.01	M. C.	0.01	0.01	<0.001	0.001
Carbon (%)				0.04	0.05			
Sulfur (%)				<0.01	<0.01			

(a) All spectrographic analysis are based on percent by weight of the solid material. Liquid samples were dried to a solid and the percent (by weight) of impurities uses the dried solids as the 100% reference.

V. EXPERIMENTAL RESULTS

A. Preliminary Solution Evaluation

The basic solution operating parameters of the nickel-cobalt sulfamate alloy system were obtained prior to physical property determinations using the techniques, equipment, and solutions presented in Section IV-A. The results obtained are discussed in the following sections.

1. Effect of Solution Nickel and Cobalt Content and the Applied

Current Density on Deposit Composition--The operating parameters required to produce any desired nickel-cobalt alloy are shown in Figures 7 and 8. Figure 8 shows that with current density variations between the 2 amp/dm²(20 ASF) and 5 amp/dm²(50 ASF) levels studied, and with solution Ni/Co ratios less than 5 and greater than 100, the deposit composition changed only 2 to 3 percent; whereas, with ratios between 5 and 100 the deposit composition was found to vary by approximately 10 percent. In all cases, at any set solution ratio, a decrease in the current density resulted in decreasing the nickel content of the deposit. It is evident from Figure 7 that the deposition of alloys containing from 5 to 35 percent cobalt will require very close control of the solution metal ratio. The data obtained supports the statements of Brenner⁽⁵⁾ that in the nickel-cobalt plating system, anomalous codeposition occurs and cobalt deposits preferentially, although cobalt is less noble than nickel. The data also indicates that no limiting deposit composition is obtained from the sulfamate base system.

Figure 7. Deposit Composition as a Function of Solution Composition at 30 ASF, 2.68 Normal

Figure 8. Effect of the Ni/Co Ratio of the Solution and Applied Current Density of Deposit Composition

2. Effect of Solution Total Metal Content on Deposit Composition--

Figure 9 shows the effect on deposit composition resulting from varying the bath metal normality from 1 to 4. The data was obtained from solutions containing a constant cobalt ratio (10 wt. %) and agrees with that presented in Brenner⁽⁶⁾ in the 1 to 3 N. region, although a reversal was obtained when the solution composition was increased to 4 normal. It also indicated that, to obtain minimum deposit composition changes with bath formulations containing approximately 10% cobalt, the total metal concentrations should be between 2 and 3.5 N.

3. Effect of Boric Acid Content and Operating Temperature on Deposit

Composition--Figure 10 shows the data obtained for two Ni/Co ratios (Ni/Co = 10 and 20) at operating temperatures of 100, 120 and 140° F. for various boric acid concentrations. The other parameters of the alloy plating solution were maintained at a constant value for both of the solution Ni/Co levels studied (pH = 4, 78.8 gm/l total metal, 30 ASF). The effect of increasing the boric acid concentration from 30 to 45 gm/l resulted in markedly different effects on the nickel content of the deposit at the two Ni/Co ranges studied. In the 70 percent nickel composition range (Ni/Co = 20) an increase in the boric acid content resulted in increasing the nickel content of the deposit. In the 55 percent nickel range (Ni/Co = 10) an increase in the boric acid content resulted in first increasing and then decreasing the nickel content of the deposit. It was also indicated that temperature variations had mixed effects on the deposit composition in the two Ni/Co ranges tested.

Figure 9. Effect of the Total Metal Content of the Solution on Deposit Composition at 30 ASF.

Figure 10. Effects of Boric Acid Concentration and Solution Temperature on Deposit Composition at Ni/Co Ratios of 10 and 20.

4. General--The magnitude and rate of change of the alloy compositions resulting from small changes in temperature, boric acid, total metal content and applied current density indicated that moderately close control of the solution variables should be maintained during a plating cycle. Because of the mixed effects some of these variables had, it was evident that extrapolation of these effects to other operating ranges was not advisable.

B. Physical Property Determination---Pure Nickel and Pure Cobalt

The physical properties of the pure metal deposits, produced from the sulfamate system, were determined to provide an adequate basis of comparison for the nickel-cobalt alloy system. The studies include the changes in the physical properties of the pure metals which result from the utilization of various solution additives in both "new" and "used" plating baths. The various physical properties determined thus far in the investigation are discussed as follows:

1. Ultimate and Yield Strength---The strength characteristics obtained from the various pure metal deposition systems are shown in Figure 11. The bath formulations used are presented in Table 2, and the bath history and deposit characteristics presented in Table 4. The data shown in Figure 11-a is included for comparison only, and was not obtained by the procedure used for all subsequent work (Section IV-B4). These tensile test panels were produced "one at a time," from a production plating solution at 5 amp/dm²(50 ASF). Further investigative work on this system was not carried out because of the large amount of applicable data available.⁽¹⁸⁾⁽¹⁹⁾⁽²⁰⁾⁽²¹⁾

The results obtained for the chloride (Cl⁻) and bromide (Br⁻) containing sulfamate systems (Figure 11-a and 11-b) are well within the strength ranges reported in the literature. The addition of N.T.S.A. (napthalene 1, 3, 6, trisulfonic acid, sodium salt) to either the chloride or bromide modified systems resulted in increasing the ultimate and yield strengths of the subsequent deposits. The yield and ultimate strengths for deposits from both systems became coincident when the heat treatment temperatures exceeded, approximately, 600° F. The N.T.S.A. modified systems (Figure 11-c

and 11-d) indicated that the strength characteristics of these deposits were also dependent upon the halogen utilized in the solution. The data which has been obtained on the modified solutions, indicate that bath life is an important factor in the "as plated" strength of the deposit. The solutions used to produce the test specimens for which the data is presented, had produced slightly stronger deposits earlier in their processing history; i.e., 155,000 psi, Br⁻ system and 165,000 psi, Cl⁻ system. This indicates probable adverse effect by certain breakdown products in the system.

The addition of Perflow to the chloride-N.T.S.A. system significantly changed the strength characteristics of the deposit, although coincident yield and ultimate strengths were again obtained with heat treatments greater than 600° F. Additional data has been obtained from this system which indicates that "as plated" ultimate strengths of 260,000 to 280,000 psi and yield strengths of 170,000 to 180,000 psi are obtained from relatively "new" solutions. The deterioration in strength with bath life, was found to proceed at a much faster rate than for the system without Perflow.

The pure cobalt deposits were found to exhibit completely different heat treated strength characteristics than any of the nickel deposits investigated. The increased strength with heat treatment above 500° F. obtained from the cobalt deposits were not expected. The photomicrographs obtained for the cobalt deposits (Figure 19) show no appreciable grain growth or change in grain structure with heat treatments up to 1150° F. The strength-temperature phenomenon observed for the cobalt deposits

Figure 11. Strength vs. Heat Treat Temperature for Pure Materials from Various Baths

TABLE 4.

BATH HISTORY AND DEPOSIT CHARACTERISTICS

Bath Type	Solution History	Deposit Appearance	Average (a) Stress (psi)	Average Sulfur Content
A	240 gal.--production solution	matte grey	+3,000 (b) to +12,000	0.001% (b)
B	76 liter--new make-up	matte grey	+7,100	---
D	76 liter--used bath (>40 amp-hr/liter)	bright	-7,500	0.0022%
E	76 liter--used bath (>40 amp-hr/liter)	bright	-8,500	0.0016%
F	68 liter--used bath (>20 amp-hr/liter)	very bright	-3,500	0.0019%
C	28 liter--new make-up	dull matte grey	---	---

(a) Spiral contractometer determination. Negative values indicate compressive stress.

(b) Typical values.

may be attributed to the hexagonal cubic transformation this metal undergoes above approximately 780° F. Crystallographic studies of the deposits, in an attempt to explain this characteristic, have not been obtained at this time.

2. Hardness and Elongation--The hardness (Figure 12) and elongation (Figure 13) properties of the pure metal deposits produced under the various conditions were of the general magnitude expected, except for the cobalt deposits. In general, the nickel deposits had higher hardness and lower elongations when produced from the solutions containing additives. The magnitude of these properties varied considerably and supported the conclusion that the halide present in the solution contributes to the physical properties of the electrodeposits.

The hardness of the cobalt deposits were found to increase, along with the strength, with increasing heat treatment temperature. The elongations were found to be approximately constant and relatively low with respect to the nickel deposits produced without organic additives at heat treatment temperatures up to 1150° F.

3. Structure of the Pure Metal Deposits--The microstructures of the pure metal deposits at various degrees of heat treatment are presented in Figures 14 through 19. A summary of the deposit structures in the as plated and at a heat treatment of 1150° F. is given in Table 5. Examination of the various microstructures resulted in the following conclusions.

- a. The addition of Perflow and/or N.T.S.A. to the nickel sulfate solution results in as plated deposits with fine, equiaxed, grain structures whereas without the additives the deposits have a medium grained, columnar structure.

- b. Heat treatment of the deposits indicates that the addition of Perflow and/or N.T.S.A. inhibits the grain growth upon recrystallization producing a fine, equiaxed grain structure as opposed to a medium size grain structure resulting from the system without additives.

Figure 14-b shows a typical kernel type growth emanating within the deposit, which was found to be more prevalent in deposits produced at current densities of 5 amp/dm²(50 ASF) than at 3 amp/dm²(30 ASF). Figures 14-a, 14-c and 15-a through 15-d show what is thought to be the effect of an abrupt current density change during deposition. Figure 17-d shows the structure of a thin specimen produced during one test. The strength and hardness properties of this deposit were well within the range obtained from standard thickness specimens and the sulfur content was not greatly different. It is thought that this structure is a result of the lower current density on this specimen. Figure 18-e shows typical "gas pits" which were obtained on some specimens. Figure 19 shows that the cobalt microstructure remains essentially unchanged throughout the heat treatment range studied.

Figure 12. Hardness vs. Heat Treat Temperature for Pure Materials From Various Baths

Figure 13. Elongation vs. Heat Treat Temperature for Pure Materials from Various Baths

TABLE 5.

NICKEL AND COBALT METAL, MICROSTRUCTURES (SUMMARY TABLE)

Figure No.	Bath Description	Metal	Comments on Microstructure	
			As Plated	1150° F. Heat Treatment
14	Sulfamate Chloride	Ni	Medium Grain, Columnar	Fine - Medium Grain, Partially Recrystallized
15	Sulfamate Bromide	Ni	Medium Grain, Columnar	Medium Grain, Fully Recrystallized
16	Sulfamate Chloride N.T.S.A.	Ni	Very Fine Grain, (One of the Finest) Equiaxed	Fine Grain, Recrystallized, Equiaxed
17	Sulfamate Bromide N.T.S.A.	Ni	Very Fine Grain, Equiaxed	Fine Grain, Recrystallized, Equiaxed
18	Sulfamate Chloride N.T.S.A. Perflow	Ni	Fine Grain, Tendency Toward Columnar Growth	Fine Grain, Recrystallized, Equiaxed
19	Sulfamate Bromide	Co	Fine Grain, Columnar	Fine Grain, Columnar (No Recrystallization)

FIGURE 14. MICROSTRUCTURE OF NICKEL DEPOSITED FROM A SULFAMATE-CHLORIDE SOLUTION (BATH A)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment 300X

FIGURE 15. MICROSTRUCTURE OF NICKEL DEPOSITED FROM A SULFAMATE-BROMIDE SOLUTION (BATH B)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 16. MICROSTRUCTURE OF NICKEL DEPOSITED FROM A
SULFAMATE-N. T. S. A. - CHLORIDE SOLUTION (BATH D)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 17. MICROSTRUCTURE OF NICKEL DEPOSITED FROM A
SULFAMATE-N.T.S.A. - BROMIDE SOLUTION (BATH E)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 18. MICROSTRUCTURE OF NICKEL DEPOSITED FROM A
SULFAMATE-N.T.S.A. - PERFLOW-CHLORIDE
SOLUTION (BATH F)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 19. MICROSTRUCTURE OF COBALT DEPOSITED FROM A SULFAMATE-BROMIDE SOLUTION (BATH C)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

C. Physical Property Determinations--Nickel-Cobalt Alloys

The physical properties of nickel-cobalt alloys containing from 0 to 22 and 45 to 100 percent nickel have been determined for the sulfamate based alloy plating system with bromide additive (Bath Type G). Ultimate strength, yield strength, hardness, elongation and microstructure of various alloy compositions were determined at 70° F., and after heat treatment to 450°, 650°, 850° and 1150° F. for deposits produced at an average current density of 3 amp/dm²(30 ASF). The properties of deposits containing between 22 and 45 percent nickel and other selective compositions are presently being determined. The physical properties thus far determined are discussed in the following sections.

1. Ultimate and Yield Strength--The strength properties of the nickel-cobalt alloy system with heat-treatments between 70° F. and 1150° F. are shown in Figures 20 and 21. The data shows that alloys with "as plated" ultimate strengths between 70,000 and 210,000 psi and yield strengths between 60,000 and 150,000 psi can be obtained from the sulfamate-bromide system. It is concluded from the data obtained that:

- a. The addition of cobalt to a nickel matrix results in an alloy of greater strength than the base material, whereas
- b. The addition of nickel to a cobalt matrix results in an alloy of less strength than the base material.

Figure 20-a and 21-a also show that the strength of the deposits with nickel compositions between 40 and 60 percent is very sensitive to small changes in composition. This observation indicated that a major microstructure transformation exists in this composition region. The photomicrographs obtained (Figures 25,

Figure 20. Ultimate Strength vs. Nickel Content of Alloy After Heat Treatment

Figure 21. Yield Strength vs. Nickel Content of Alloy After Heat Treatment

26 and 27) show that such a transformation does occur. It is evident from the data in Figures 20 and 21 that where strength and hardness are determining factors, nickel-cobalt alloys, or pure cobalt should be considered for electroforming if heating up to 1150° F. is involved.

2. Hardness--The hardness properties of the electrodeposited nickel-cobalt alloys are shown in Figure 22. The general shape of the hardness curves reflects the strength data obtained for the alloys, except in the 70 to 90 percent nickel range. The data indicates that for all test temperatures, a microstructure change or transformation also occurs in the 70 to 90 percent nickel composition range. The ultimate and yield strength data did not show as pronounced a variation in this region.
3. Elongation--The elongation data for the electrodeposited nickel-cobalt alloys are shown in Figure 23. The elongation data was considered most unusual in nature; in that it shows that decreasing strength with heat treatment is not accompanied by a regular increase in elongation. The curves for 850° and 1150° F. (Figure 23-d and 23-e) are presented as the best average curve for the data obtained. The hardness data (Figure 22) does lend some support to curves of this general shape.

Figure 22. Hardness vs. Nickel Content of Alloy After Heat Treatment

Figure 23. Elongation vs. Nickel Content of Alloy After Heat Treatment

4. Structure of the Nickel-Cobalt Alloy Deposits--Figures 24 through 31 show the microstructures of the nickel-cobalt deposits at various degrees of heat treatment. The deposit structures in the as plated and at a heat treatment of 1150° F. are presented as a composite summary in Table 6. Evaluation of the microstructures resulted in the following conclusions.

- a. Alloys containing from 0 to 22% nickel are columnar in structure and undergo no recrystallization with heat treatments up to 1150° F.
- b. Alloys containing around 53% nickel are of a lamellar structure in the as plated condition and undergo fine grain recrystallization with heat treatments at 1150° F.
- c. Alloys containing from 70 to 80% nickel are in a columnar-lamellar transition range in the as plated condition and result in an increasing grain size with nickel content, in the recrystallized heat treated condition.
- d. Alloys containing 83% nickel have a modified columnar, as plated structure which changes very slightly with heat treatments of 450° F. to 1150° F.
- e. Alloys containing 95% nickel have very nonuniform structures in the as plated condition. Complete recrystallization occurs at 1150° F.

Figures 24-a, 25-a, 25-b, 26-b and 26-c show the effects that initial surface irregularities have on the growth pattern of the alloy deposits. Figure 28 shows evidence of a deposit growth change occurring after approximately one fourth of the final thickness was obtained. No gross current density, or solution composition changes were observed during this test and the cause

for the abnormality is unknown at this time. Figure 30 also shows evidence of a structure change occurring near the end of the plating cycle. Figure 30-e includes a cross section of a typical "gas pit," although very few were observed on the deposits produced in the alloy plating system. It should be noted that the strongest, hardest deposits produced from the alloy system had microstructures which were lamellar in nature. The microstructures also support physical property data obtained in that structure changes are observed where gross changes in physical properties appear.

TABLE 6.

NICKEL-COBALT ALLOY MICROSTRUCTURES (SUMMARY TABLE)

Figure No.	Nickel Content (%)	Comments on Microstructure	
		As Plated	1150° F. Heat Treatment
24	17	Medium Grain, Columnar	Medium Grain, Columnar (No Recrystallization)
25	22	Medium Grain, Columnar	Medium Grain, Columnar (No Recrystallization)
26	53	Highly Lamellar	Fine Grain, Recrystallized, Equiaxed
27	70	Fine Grain, Slight Lamellar Tendency	Fine Grain, Recrystallized, Equiaxed
28	73	Fine Grain, Lamellar with Very Fine Columnar Tendency	Fine - Medium Grain, Fully Recrystallized
29	80	Medium Grain, Columnar with Slight Lamellar Tendency	Medium Grain, Fully Recrystallized
30	83	Fine and Medium Grain, Modified-Columnar	Fine and Medium Grain, Partially Recrystal- lized
31	95	Medium and Large Grains, Columnar (Non-Uniform)	Medium Grain, Fully Recrystallized

FIGURE 24. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (17% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 25. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (22% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 26. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (53% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 27. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (70% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 28. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (73% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 29. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (80% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

FIGURE 30. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (83% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment 300X

FIGURE 31. MICROSTRUCTURE OF NICKEL-COBALT ALLOY (95% Ni)

a. As Plated Deposit. 300X

b. 450°F. Heat Treatment. 300X

c. 650°F. Heat Treatment. 300X

d. 850°F. Heat Treatment. 300X

e. 1150°F. Heat Treatment. 300X

D. Bath Operations

General comments on the operations of the various solutions investigated can be stated as follows:

1. Pure Metal Deposits

- a. Good solution filtration and agitation must be maintained in the N.T.S.A.-Perflow system because of the continued breakdown of these additives in this system.
- b. Installation and utilization of a N.T.S.A. or N.T.S.A.-Perflow system should include a scheduled deposit testing program so that the physical properties are within the range desired.
- c. The analytical procedures presented in Appendix Section 1 have proved adequate in maintaining the additive concentrations in the N.T.S.A. and N.T.S.A.-Perflow systems.
- d. The utilizations of N.T.S.A. and Perflow in the nickel sulfamate system does not result in unacceptable deposits. They produce electroformable deposits which are stronger, harder, and have finer grain structures than are obtained from the basic system. In addition the deposits are compressively stressed, do not contain excessive sulfur (Table 4) and do not degrade with temperature up to 1150° F. at unacceptable rates.

2. Nickel-Cobalt Alloy Deposits

- a. The utilization of a split anode system (Figure 1) works fairly well with solution Ni/Co ratios of 5 to 30 but controlled, selective, anode corrosion is difficult with higher ratios. The metering system (Figure 2) is considered the best overall operating technique and is recommended for general use in this system.
- b. Cathode efficiencies for all the alloy deposition ranges

have not been determined to date, but determinations at deposit compositions of 30 to 75 percent nickel have all exhibited cathode efficiencies between 97 and 100 percent.

- c. Good solution filtration and agitation should be maintained with the alloy plating system to reduce solution contamination and deposit defects.
- d. Analytical control of the system can be maintained by the procedures listed in Appendix Section 1. Although, with high solution metal ratios an ion-exchange, colorimetric, or polarographic procedure for cobalt is desired.
- e. Alloy deposit analysis are very readily and accurately obtained by the x-ray fluorescence method described in Appendix Section 2. The ion-exchange method will provide just as accurate analysis but requires considerably more laboratory time.
- f. Leveling, stress reducing and hardening agents for the alloy system are under investigation at this time to determine if even higher strength deposits may be obtained and maintained at elevated temperature.

VI. CONCLUSIONS

Nickel-cobalt alloys can be produced with a wide range of physical properties which depend upon the alloy composition and the degree of heat treatment incorporated. Alloy electroforms having ultimate strengths exceeding 220,000 psi with yield strengths exceeding 160,000 psi have been frequently produced. The alloy electroforming process is readily operable with reasonable analytical control. The effects of current density variations resulting from complex electroform shapes may require special anoding or solution and operating modifications so that a deposit having uniform properties is obtained. Investigations to date have indicated that the alloy system is capable of producing thicknesses comparable to the standard nickel sulfamate system.

The use of cobalt in electroforming applications appears promising because of the retention of the physical properties at high temperatures. To date, ultimate strength is limited to 120,000 psi with a yield strength of 75,000 psi using the sulfamate system and a bromide additive. The utilization of other solution additives in the cobalt system may produce deposits with improved physical properties that are maintained up to the recrystallization temperature.

The use of selective additives in the nickel sulfamate system results in deposits with greater strengths, higher hardness and lower elongations than are produced from the basic system. Deposits having ultimate strengths from 140,000 psi to 260,000 psi, and yield strengths from 120,000 psi to 170,000 psi have been produced from organic modified systems. In addition, these properties are enhanced, somewhat, by low temperature heat treatments in the neighborhood of 400° F.

The dimensional stability of the deposits produced from the alloy and modified nickel systems appears satisfactory, however, this property has not been specifically evaluated.

The exact type of deposit incorporated into any electroforming application will be dictated by the end requirements of the design. The data presented in this report should provide a wider range of properties which can be incorporated into specific electroforming applications, especially of the simpler design types.

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VIII. APPENDIX

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SECTION 1.

Solution Chemical Analysis Procedures

A. Total Metal Content (Ni + Co)

1. Pipette 10 ml plating solution into a 500 ml volumetric flask and dilute to volume with distilled water. (Stock Solution)
2. Pipette 15 ml of stock solution into a 250 ml beaker containing approximately 75 ml distilled water.
3. Add 1.0 ml (fresh) murexide indicator, mix thoroughly and adjust pH to approximately 8.0 with 50 (vol. percent) ammonium hydroxide.
4. Titrate to a red-violet end point with 0.1M E.D.T.A. (NOTE: Maintain pH near 8.0 during titration. End point must be stable for more than one minute.)
5. CALCULATIONS:

$$(\text{ml } 0.1\text{M E.D.T.A.})(19.6) = \text{gm/l of total metal (Ni + Co)}$$

B. Nickel Content

1. Pipette 15 ml stock solution (prepared in A-1) into a 400 ml beaker containing 0.5 gram ammonium nitrate and approximately 35 ml distilled water.
2. Adjust pH to 2.0 with dilute nitric acid.
3. Add exactly 10 ml 0.1M E.D.T.A. solution, mix and readjust pH to 2.0.
4. Add sufficient crushed ice (made from distilled water) to bring temperature to 32° F. (0° C.) and to maintain this temperature during titration.
5. Add 5 drops, pyrocatechol violet indicator and titrate to a red-violet end point with 0.05M bismuth nitrate.

6. CALCULATIONS:

$$1.0 - (0.05)(\text{ml Bi}(\text{NO}_3)_3) (195.6) = \text{gm/l nickel}$$

C. Nickel Bromide or Magnesium Chloride Content

1. Pipette 5.0 ml of bath solution into a 250 ml erylenmeyer flask containing 100 ml of distilled water.
2. Add 1 ml of 2 percent sodium chromate solution and titrate with 0.1 N silver nitrate solution to a pink end point.

3. CALCULATIONS:

a. ml of $\text{AgNO}_3(2.185) = \text{gm/l NiBr}_2$

b. ml of $\text{AgNO}_3(0.952) = \text{gm/l MgCl}_2$

D. Boric Acid Content

1. Pipette 25 ml of inverted sugar reagent* into a 150 ml beaker containing 20 ml of distilled water. (NOTE: If solution is yellow or orange in color, add one or two drops of 0.2 N sodium hydroxide solution until the color is deep red.)
2. Pipette 5.0 ml of the bath solution** into the adjusted reagent.
3. Titrate with 0.2 N sodium hydroxide to a deep red end point.
4. CALCULATIONS:

$$\text{ml NaOH}(2.405) = \text{gm/l of H}_3\text{BO}_3$$

* Dissolve 1000 grams of cane sugar or CP sucrose in 330 ml of distilled water. Boil for several minutes until the solution is clear, and quickly add 25 ml of 1 N sulfuric acid and stir for 30 seconds. Allow the solution to cool and add 0.1 percent Cresol Red to the inverted sugar solution. Add a solution of sodium hydroxide containing 1.2 grams per 600 ml to the mixture and mix thoroughly.

** If the bath pH goes below 4.0 a second sample should be run without using the inverted sugar reagent. Subtract the ml of 0.2 N sodium hydroxide used in this determination from that obtained during the analysis so that the corrected quantity of 0.2 N sodium hydroxide is used.

E. N.T.S.A. Content

1. Prepare at least 2 standards by accurately weighing out pure N.T.S.A. and dissolving in distilled water. (NOTE: The standards may contain 7.5000 and 11.0000 gm/l respectively.) (Solution "A")
2. Pipette 20 ml of "A" into a 1000 ml volumetric flask and dilute to volume with distilled water. (Solution "B")
3. Pipette 5 ml of "B" into a 250 ml volumetric flask and dilute to volume with distilled water. (Solution "C")
4. Transfer 4 to 4.5 ml of "C" to a one centimeter quartz cuvette and determine the absorbance or transmittance at 284 m μ .
5. Obtain absorbance and transmittance values at 284 m μ for unknown samples and determine plating bath concentrations from a standardization curve.

F. Perflow Concentration (Determination in the Presence of N.T.S.A.)

1. Pipette a 5 ml sample of the bath into a 125 ml separator funnel and add 10 ml of distilled water. Place a plug of surgical cotton in the lower stem of the separatory funnel.
2. Extract the solution with 2 ml and 15 ml portions of A.R. grade chloroform (CHCl_3). Combine extracts in a 100 ml volumetric flask and dilute to volume with chloroform. Determine absorbance or transmittance at 276 m μ for unknown and determine preflow concentration from a standardization curve.

SECTION 2.

Deposit Analysis Procedures

A. Ion Exchange - E.D.T.A. Titrate Method for Nickel and Cobalt

1. Dissolve approximately 0.4 gram sample of nickel-cobalt alloy in a 250 ml beaker containing 75 ml of conc. HCl and 10 ml of conc. HNO_3 .
2. Heat to give a moderately fast reaction and maintain temperature and volume until the sample is completely digested.
3. Evaporate to dryness on a steam bath, cool and add water and 1 ml of conc. HCl. Heat slightly to completely dissolve the residue and transfer to a 100 ml volumetric flask and dilute to volume.
4. Pipette 10 ml of this solution into a 50 ml beaker and add 19.5 ml of conc. HCl. Mix thoroughly and wash into Ion Exchange column reservoir with 5 ml washings of 8.0M HCl. (NOTE: Ion Exchange column contained in 1.2 cm. I.D. tube with 28 cm. of resin, Dowex 1-X8.)
5. As sample passes through column, wash thoroughly with 8.0M HCl. Do not let column run dry. The sample thus passed through the column will contain all the nickel in the sample.
6. The cobalt contained on the column can be removed from the resin by washing with 0.1M HCl.
7. The pure nickel and pure cobalt effluents are then analysed in the following manner:
 - a. Place effluents on a steam table and evaporate to dryness.
 - b. Add 150 ml of deionized water and 10 drops of conc. HCl. Adjust pH to 5.2 using solid hexamethylenetetramine and conc. HCl.

- c. Add an excess of 0.01M E.D.T.A. from a burette and 6 drops Xylenol orange indicator.
- d. Back titrate with 0.01M $\text{Pb}(\text{NO}_3)_2$ to orange-yellow end point.
- e. CALCULATIONS:

$$\frac{[(\text{ml EDTA} \times M_1) - (\text{ml Pb}(\text{NO}_3)_2 \times M_2)] \times 58.71}{\text{Sample Wt (gm)}} = \% \text{Ni}$$

$$\frac{[(\text{ml EDTA} \times M_1) - (\text{ml Pb}(\text{NO}_3)_2 \times M_2)] \times 58.94}{\text{Sample Wt (gm)}} = \% \text{Co}$$

where:

M_1 = molarity of EDTA

M_2 = molarity of $\text{Pb}(\text{NO}_3)_2$

B. X-Ray Fluorescence Analysis for Nickel and Cobalt

1. Dissolve approximately 0.4 gram sample of nickel-cobalt alloy in a 250 ml beaker containing 75 ml of conc. HCl and 10 ml of HNO_3 .
2. Heat to digest and then evaporate to dryness on a steam table. Cool, add water and 1 ml of conc. HCl.
3. Heat slightly to completely dissolve residue and transfer to a 100 ml volumetric flask and dilute to volume.
4. Remove approximately 2 ml of solution and place in a plastic sample cup sealed with a sheet of 0.00025 inch mylar.
5. Place the specimen in the sample chamber of the x-ray spectrograph and bombard with 50 KV x-rays from a tungsten target x-ray tube.
6. The resulting α fluorescence from the nickel and cobalt are analysed by a scintillation detector counting system.
7. The percent nickel in the sample is obtained from a standardization curve utilizing the count rate ratio ($K_{\alpha} \text{Ni}/K_{\alpha} \text{Co}$) vs. percent nickel in the sample.

SECTION 3.

Schematic of Current Divider

Figure 32

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