THE PREPARATION OF ELECTROLYTIC DEPOSITS OF NICKEL FOR THE STUDY OF PHYSICAL PROPERTIES OF THE METAL

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THE PREPARATION OF ELECTROLYTIC DEPOSITS OF NICKEL FOR THE STUDY OF PHYSICAL PROPERTIES OF THE METAL

By

WILLIAM MARTIN KING

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INTRODUCTION

A systematic and comprehensive search of the literature has shown that there has been no standardization of tests to illustrate the effects of impurities in nickel plating solutions. Further search showed that in no case was the purification of the starting solution described before the addition of impurities. The results have been described but the methods of attaining these results have not been sufficiently set forth to enable an operator to reproduce them.

This paper describes a method for the preparation and purification of nickel plating solutions, plating of the panels, addition of impurities, standard tests to be performed on the deposits and the evaluation of these tests. In all cases the additions of impurities was made to a nickel plating solution the purity of which was established analytically and spectroscopically.

Four nickel plating solutions, two grey solutions, an alloy type bright solution and an organic type bright solution were selected for this investigation. For the grey solutions the Watts type was chosen and operated at a pH of 2.2 and 5.2. For the alloy type a nickel-cobalt (18%) solution as described by the Weisberg-Stoddard patent was chosen, and for the organic type a solution as described by the Schlotter patent.

The physical properties to be investigated in deposits from these solutions were chosen from the either known or suspected

effects of impurities. The methods of testing were chosen for simplicity and ease of testing in order that industrial personnel could make on the spot checks. The tests of physical properties which were decided upon are appearance, adherance, salt fog corrosion resistance, ductility, hardness, throwing power and efficiency.

All deposits containing impurities are compared to the deposit from pure solutions on a relative basis using the pure deposit as a standard. There is no attempt made to cross evaluate between the four nickel solutions. As each impurity is studied, upper and lower limits of contamination are established by preparing a series of panels containing an increasing amount of the impurity. When a deposit becomes obviously unusable, it was deemed not necessary to investigate concentrations of impurities above this point. The limits are established by the project committee from this series of panels.

The analysis of impurities in nickel plating solutions used are those developed by Dr. Earl Serfass, Professor of Analytical Chemistry at LeHigh University, under Project No. 2 of the American Electroplater's Society.

PREPARATION AND PURIFICATION OF SOLUTIONS

The four nickel plating solutions used in this investigation are listed in the following tables. The Watts type nickel plating solutions are used for producing the grey nickel deposits.

Table No. 1.

Watts type nickel plating solution		
Nickel sulfate	240 grams/liter	32 oz/gallon
Nickel chloride	45 "	6 "
Boric acid	30 "	4 "
Temperature	50° C.	122° F.
pH (electrometric)	2.2 and 5.2	
Current density	40 amperes per square foot	

The bright nickel solutions are an alloy type as described in U. S. patent No. 2,026,718 by Weisberg and Stoddard and modified as shown in Table No. 2. The organic type solution is described in U. S. patent No. 1,972,693 by M. Schlotter and modified as shown in Table No. 3.

Table No. 2.

Nickel-Cobalt (18%) alloy type		
Nickel sulfate	240 grams/liter	32 oz/gallon
Nickel chloride	45 "	6 "
Boric acid	30 "	4 "
Nickel formate	45 "	6 "
Cobalt sulfate	15 "	2 "
~~Ammonium sulfate~~	~~2.5~~ "	~~0.33~~ "
Formaldehyde	2.5 "	0.33 "
Temperature	55°C	132°F
pH (electrometric)	3.75	
Current density	40 amperes per square foot	

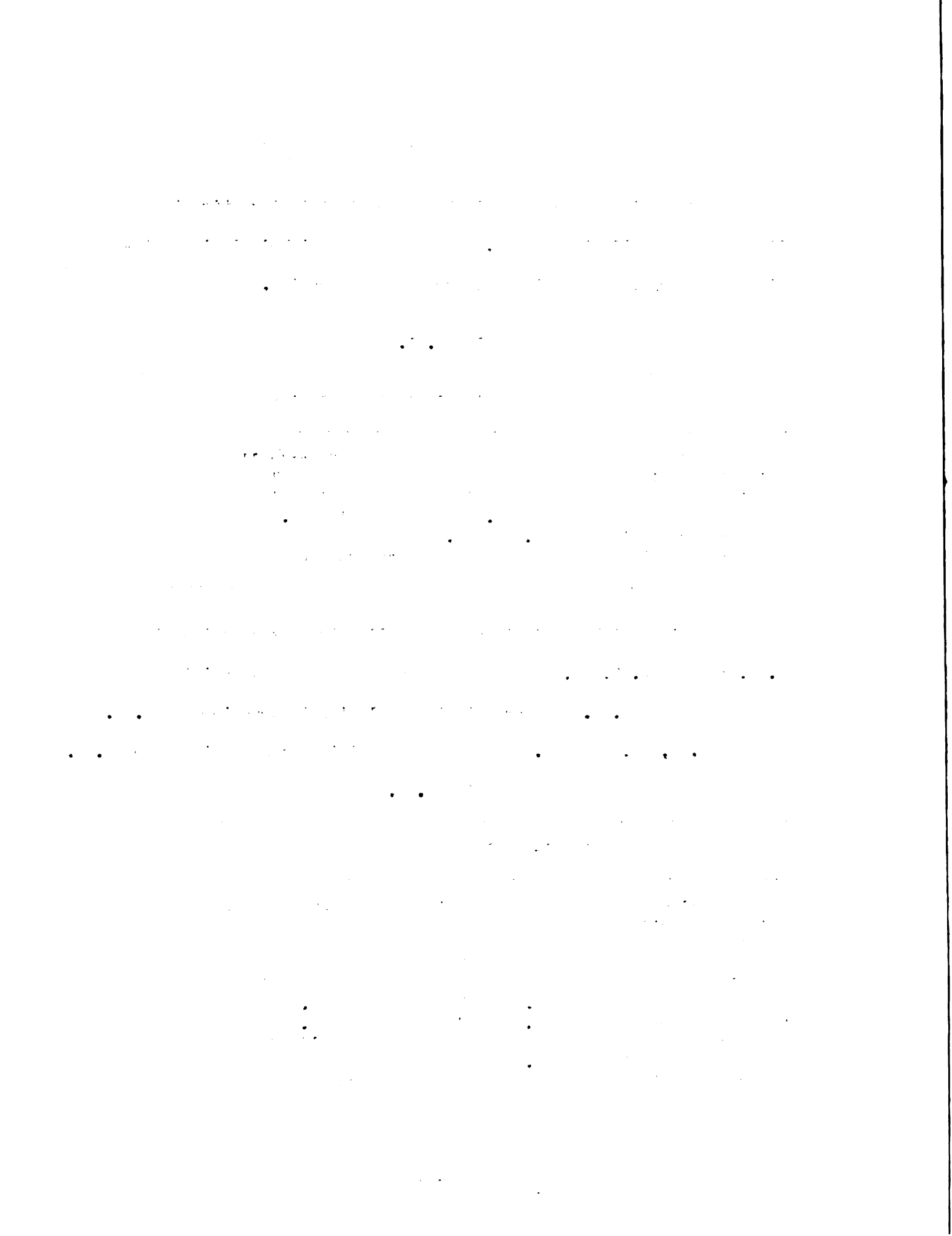


Table No. 3.

Organic type solution		
Nickel sulfate	262.5 grams/liter	35 oz/gallon
Nickel chloride	60 "	8 "
Boric acid	34 "	4.5 "
Nickel benzene disulfonate	7.5 "	1 "
Triaminotolyldiphenylmethane	0.14 ml/liter	
Temperature	55° C.	132° F.
pH (electrometric)	3.2	
Current density	40 amperes per square foot	

The plating solution is made up in a twenty liter pyrex glass container heated by a pyrex steam coil immersed in the solution. Agitation is accomplished by a single pyrex coil immersed in the solution and perforated at 2 cm. intervals allowing air to escape thus agitating the solution. The air and steam coils rest on the bottom of the container. The air is purified by passing through a 25 mm. column 4 feet long, filled with a good commercial grade of activated carbon with cotton plugs at either end. This column is recharged before each purification.

The high pH precipitation of metallic impurities is accomplished by the addition of a slurry of freshly precipitated nickel carbonate. This is added in sufficient quantity to raise the pH of the solution to 5.5-5.6 in a period of three hours at a temperature of 70-75° C with air agitation as previously described. The freshly precipitated nickel carbonate is prepared by adding a hot concentrated solution of c.p. nickel sulfate to a 25% solution of c.p. sodium carbonate.

When the solution stops bubbling, it is necessary to stop adding the nickel sulfate but to continue stirring for a few minutes. The precipitate is filtered off through a large Buchner funnel. The nickel carbonate is transferred to a large-mouth gallon bottle and the bottle filled 3/4 full with distilled water. The bottle is shaken violently, making sure all the lumps of nickel carbonate are broken up. The precipitate is allowed to settle, and the liquid decanted off. This washing is repeated four times. Finally the bottle is filled 3/4 full with distilled water and shaken. This slurry is then added to the plating solution for the high pH precipitation.

The plating solution is held at the previously described pH, temperature and agitation for a period of 24 hours. It is then filtered through a Buchner funnel with a filter paper and $\frac{1}{4}$ inch of gooch asbestos. The pH of the plating solution is adjusted to its operating range with c.p. sulfuric acid.

The plating solution is returned to the 20 liter pyrex jar for further purification by the electrolytic method for removal of metallic impurities. An anode of electrolytic nickel is placed in the solution on one side of the jar while a corrugated cathode of nickel plated steel is placed on the other side. This cathode is prepared by taking a strip of tin can stock 7"x14" and beginning at one end, making alternate 90° bends each $1\frac{1}{2}$" along the strip. The distance is adjusted between the peaks of the bends to 2 inches apart. The cathode is placed in the solution with corrugations running vertically and on

the opposite side of the jar from the anode. A cathode prepared in this manner will give a projected area of approximately 0.40 square feet. The area of the cathode is not critical, but designed to fit the container used.

An ammeter and carbon-pile rheostat are used to adjust the current through the solution. Temperature is maintained at 70-75°C. with strong agitation with air which was purified as previously described. The current is passed through the solution at a current density of 5 amperes per square foot of projected area of cathode giving a cathode current density of 2-7 amperes per square foot. The current is passed until purification is complete as determined by spectroscopic analysis. It has been found that about 100 ampere hours per gallon of solution will remove the heavy metal concentrations to spectroscopic traces.

Upon completion of the electrolytic purification the anode and cathode are removed from the solution. The organic impurities are removed by the addition of about 7.5 grams per liter of activated carbon of a good commercial grade which has proven to be reliable. The solution is kept at a temperature of 70-75°C. with violent purified air agitation for a period of 24 hours. It is then filtered through a Buchner funnel coated with a filter paper and $\frac{1}{4}$ inch mat of gooch asbestos. Upon completion of the filtration the pH is adjusted to the operating range and stored in a 20 liter glass bottle.

In the preparation of a stock solution of the Watts type, a good commercial grade of nickel sulfate, c.p. nickel chloride and c.p.

boric acid are dissolved in distilled water, in the proportions as shown in Table No. 1, to make 20 liters. The solution is then given a high pH precipitation, an electrolytic purification and an activated carbon treatment as described above. After filtration and pH adjustment the solution is ready for use as a pure stock solution.

In the preparation of a stock solution of the Ni-Co (18%) type, the nickel sulfate, nickel chloride, and boric acid are dissolved in distilled water, in the proportions as described in Table No. 2, to make 20 liters. After the solution is given a high pH precipitation treatment, filtered and the pH adjusted, nickel formate of a good commercial grade, c.p. cobalt sulfate, and c.p. ammonium sulfate are added. The electrolytic purification is then carried out. The solution is next treated with activated carbon, filtered and the pH adjusted to the operating range. Formaldehyde of a c.p. grade is then added and the solution is set aside for stock use.

In the preparation of a stock solution of the organic type, the nickel sulfate, nickel chloride, boric acid and the nickel benzene disulfonate of a good commercial grade are dissolved in distilled water in the proportions as shown in Table No. 3, to make 20 liters. The solution is then given a high pH precipitation, pH adjustment, electrolytic purification, activated carbon treatment and filtration as described above. The pH is adjusted to the operating range and a flat nickel plated steel cathode and a electrolytic anode are then introduced into the solution. Nickel is deposited at a current density

of 40 amperes per square foot for 4 hours at a temperature of 55° C. with purified air agitation. The pH of the solution is readjusted, triaminotolyldiphenylmethane of a good commercial grade is added in the amount shown above, and the solution is set aside for stock use.

As the need arises, other methods of purification will be studied.

The supplies for nickel plating, chemicals and anodes were supplied through the courtesy of the Hanson-VanWinkle-Munning Company, Udylite Corporation and the Harshaw Chemical Company.

PREPARATION OF NICKEL PLATED PANELS

The steel used for this project was low-carbon, cold rolled tin can stock of 0.01" thickness supplied to us through the courtesy of the Bethlehem Steel Corporation. This steel has an R.M.S. value of 10 as determined by means of a model SA 2 Brush Surface Analyzer. The oiled steel is protected from corrosion by storage in an air-conditioned, low relative humidity, constant temperature room.

The strip steel is cut to a standard size of 2"x8". A lip of $1\frac{1}{4}$" is formed by bending the lower edge of a 2"x8" panel 90° in a special bending clamp. This clamp consists of two pieces of $\frac{1}{4}$" nickel plated steel $1\frac{1}{4}$" wide and 4" long, tightened by two thumb screws 3" apart. A line is scribed across the panel parallel to and $3\frac{1}{2}$" from the bend. This gives an area of 0.08 square feet of surface, the front of the panel and the upper and lower side of the lip, to be plated. The bent cathode was used in preference to a straight panel or a Hull cell type panel as this type cathode is best suited for the physical measurements made thereon.

The prepared panel is degreased with carbon tetrachloride, stamped with numbering dies below the scribed line and put through the cleaning cycle preparatory to plating. The cleaner composition is as shown in Table No. 4.

Table No. 4.

Electro-cleaner composition		
Sodium hydroxide	21 grams/liter	2.81 oz/gallon
Sodium metasilicate	15 "	2.01 "
Tri-sodium phosphate	18 "	2.41 "
Sodium carbonate	6 "	0.80 "
Temperature	80°C	167°F.
Current density	75 amperes per square foot	

This cleaner is made up in 2 liter volumes fresh daily.

The tank employed for the cleaning of the panels is a 2 liter pyrex beaker lined with a strip of tin can stock 7" high. This circular sheet of steel is the cathode. The steel panel to be cleaned is placed in the center of the beaker, made the anode, and current passed for 2 minutes. The panel is removed from the cleaning tank, rinsed in water and observed for water breaks, particularly in the bend of the panel. The operation is repeated until the panel is satisfactorily cleaned. It is then given an acid dip in 20% hydrochloric acid for 2 minutes, followed by two running water rinses, the latter being distilled water.

The plating apparatus as shown in Figure No. 1 consists of a copper water bath with a composition board cover. The cover has four rectangular holes to provide for insertion of one-liter rectangular pyrex jars which measure 3"x5½"x5½". Opposite each hole is a knurled nut on a machine screw which provides the negative connection to the plating solution. All four negative connections are connected in

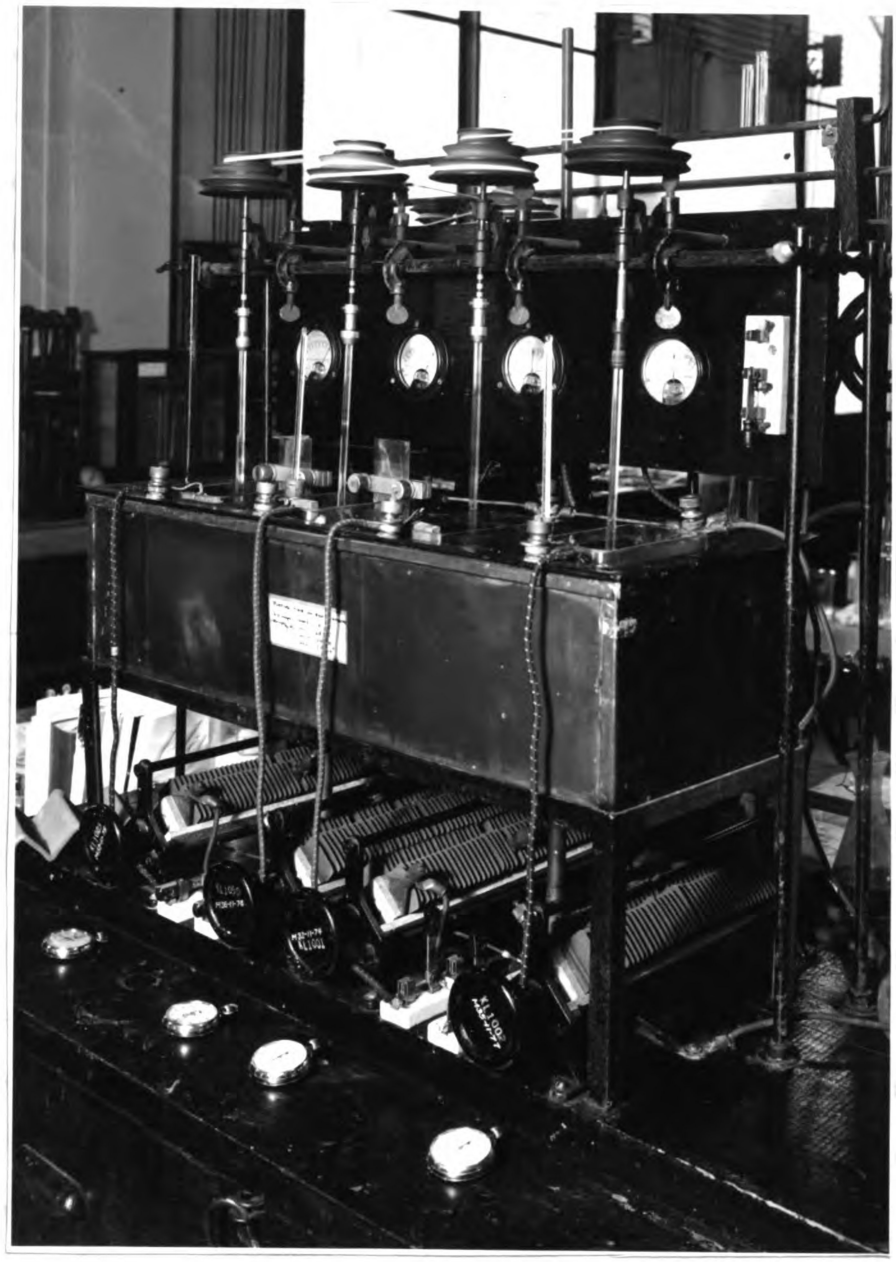


Figure No. 1 - Plating Apparatus

parallel directly to the negative bus-bar through a double throw knife switch which can be thrown to supply either $7\frac{1}{2}$ or 15 volts to this circuit. From the positive bus-bar there are four direct leads to the four ammeters on the ammeter board. The other leads from the ammeters go to the four carbon-pile rheostats provided with iron cooling fins. From the rheostats, leads go to four double throw knife switches which are provided on one side with connection to the anodes of the four baths, and on the other side with connection to four resistances which are approximately the same resistance as the resistance of the nickel plating solutions. The resistances are then connected to the negative bus-bar. Along the front of the top board, opposite each plating bath, screw connections are provided for the anodes. This arrangement allows separate control for each plating solution. The resistances connected in series with the rheostats are always thrown into the circuit when the solutions are not being used. Thus the same amount of current is flowing through the rheostats all the time whether the plating bath is in operation or not. By this means it is possible to maintain a constant flow of current to the plating solutions.

Above each tank is suspended a pulley provided with nickel plated chucks for fastening low-pitch, propellor-type glass stirring rods. The stirring rod is placed midway between the anode and cathode in the solution and 1" from the bottom of the plating bath and are electrically driven, at a constant speed of 333 revolutions per minute.

The blades of the propellors are round in shape, 5/8" long and $\frac{1}{2}$" wide (widest point), constructed of 7 mm. pyrex glass rod. The pitch of the blades on the glass stirring rods is 20° from the horizontal. The lowest amount of agitation was used that was deemed necessary to maintain uniform conditions in the solution. This rate of agitation was measured and found to be substantially 4 feet per minute of solution movement past the cathode surface. The rate was measured with the aid of a few small sawdust particles in the plating tank containing the anode, cathode and distilled water to allow observation of movement of the sawdust particles as they travelled past the cathode. This rate was adjusted by means of the propellor to give 4 feet per minute of agitation. The solution thus measured traveled vertically down past the cathode.

The milled anodes, 2" wide, 5/8" thick and $5\frac{1}{2}$" long, are placed in the pyrex jar so that the bottoms of both the anode and bent cathode are on the same level. The distance between the anode an cathode is 5" with the cathode adjusted so that the back of the panel is $\frac{1}{4}$" away from the jar to allow a thin plate of nickel to be deposited on the back to prevent iron contamination of the bath by dissolving of the steel panel. The cathode is supported in the solution by means of a clamp which rests on the top edge of the plating jar. This clamp is constructed of nickel plated $\frac{1}{2}$" steel, 5/8" wide and 4" long with two bolts $2\frac{1}{2}$" apart to allow the panel to be clamped tightly. The panel is adjusted to the correct height in the solution by immersing

to the scribed line. Connection is made by means of a copper wire which is permanently attached to the clamp. The anodes were bagged in high quality cotton anode bags.

The temperature of the water bath is maintained by two Bunsen burners. It is convenient to have one burner adjusted to produce a hot flame for major temperature changes and the other adjusted with a lower flame to keep the water bath at constant temperature for long periods of time.

After the cleaning cycle, the panel is immediately placed in the plating solution and plated at a current density of 40 amperes per square foot. (This choice of current density is explained later). The concentration of impurity under investigation is maintained by reference to depletion curves of that impurity at a current density of 40 amperes per square foot from the nickel bath in use. The depletion rate data is obtained for each of the four nickel solutions by electrolysis at a current density of 40 amperes per square foot from the solution containing the upper limit of contamination. The electrolysis is maintained until the lower limit of contamination has been passed. Samples are taken at intervals and analyzed for impurity concentrations. Curves are constructed and when a solution in operation containing an impurity has been depleted by 10% of the impurity present, a nickel solution containing a known concentration of the contaminant is added in sufficient quantity to replace the 10% lost by its electrolytic removal. The contaminated nickel solutions are

analyzed for impurity concentration at the end of each 60 minutes of plating time.

The pH of the nickel solutions is adjusted to the operating range before plating and this pH is maintained by frequent checks. A Beckman electrometric pH meter is used for this purpose.

A temperature of 50° C. (122°F.) is used for the Watts type nickel solutions, and a temperature of 55°C. (131°F.) for the bright nickel solutions of the organic and alloy type. The plating solutions were filtered before use daily.

After plating is completed, the panel is removed from the solution, rinsed in running tap water and distilled water and wiped dry with a clean cheese cloth. The dry panels are stored in a large dessicator containing calcium chloride.

EVALUATION OF PROPERTIES

A series of physical measurements to determine the effects of impurities on nickel deposits was established by the project committee. A standard operating procedure is followed in the testing of all panels for appearance, adherence, salt spray corrosion resistance, ductility, hardness, throwing power and efficiency of the bath. The number of panels prepared for each concentration of impurity in the nickel solution is kept to a minimum by utilizing panels of the same thickness for the tests requiring equal deposit thicknesses. In this manner some panels are used for more than a single test.

The current density of 40 amperes per square foot was established as this is within the operating range of the four nickel solutions under the conditions established for the tests and further, because it is a widely used value.

The vertical portion of a bent cathode was sectioned as in Figure No. 2, and examined microscopically for deposit thickness. The results of this examination are as shown by Figures No. 3 and 4. These curves show that this current density produces a deposit that is equal in thickness throughout the center portion of the panel as determined on a research metallographic microscope. The deposit increases in thickness towards the edge and decreases in thickness near the bend of the panel. In all tests requiring known thickness of the nickel deposit, the center portion of the plated panels is used.

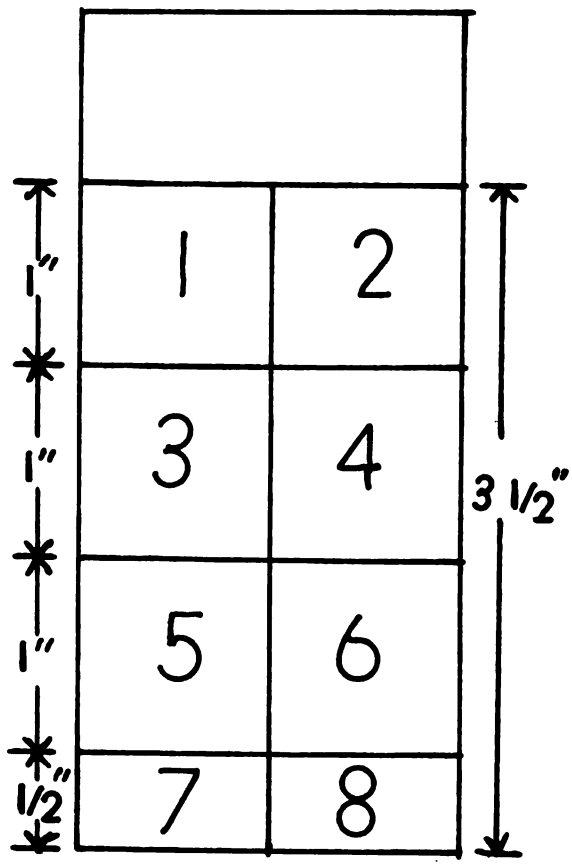
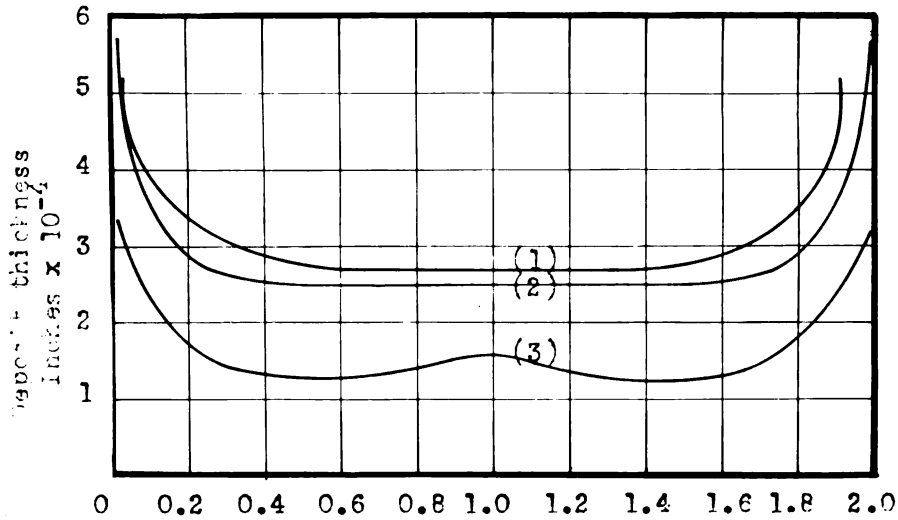
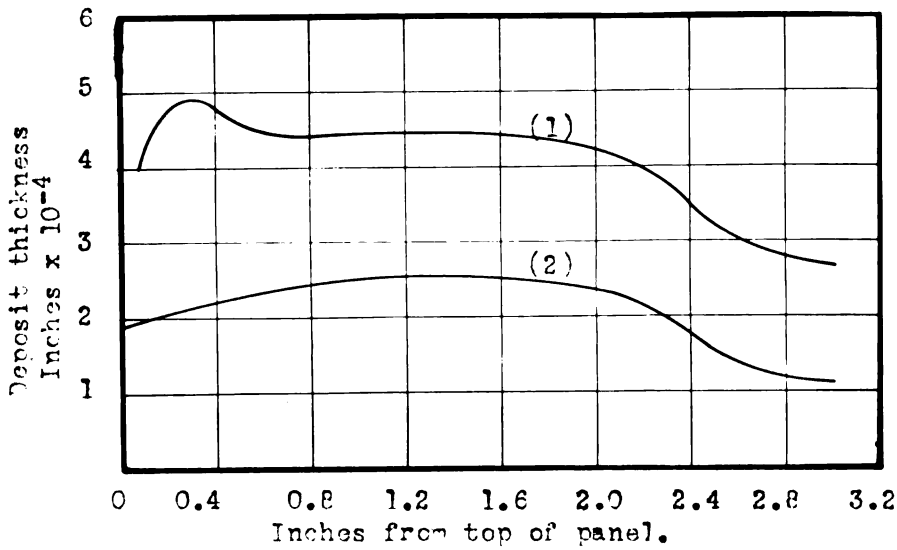


Figure No. 2 - Method of sectioning vertical portion of bent cathode for thickness measurements.



re No. 3 - Distribution of nickel on a 0.0003" panel.

Between sections 1 & 2 and 3 & 4
(2) Between sections 3 & 4 and 5 & 6
(3) Between sections 5 & 6 and 7 & 8



igure No. 4 - Distribution of nickel on a 0.0003" panel.

(1) Along edge of panel
(2) Down center of panel.

To study the range of current densities produced on the lip of the bent cathodes, 0.002" panels were plated from the four purified nickel solutions.

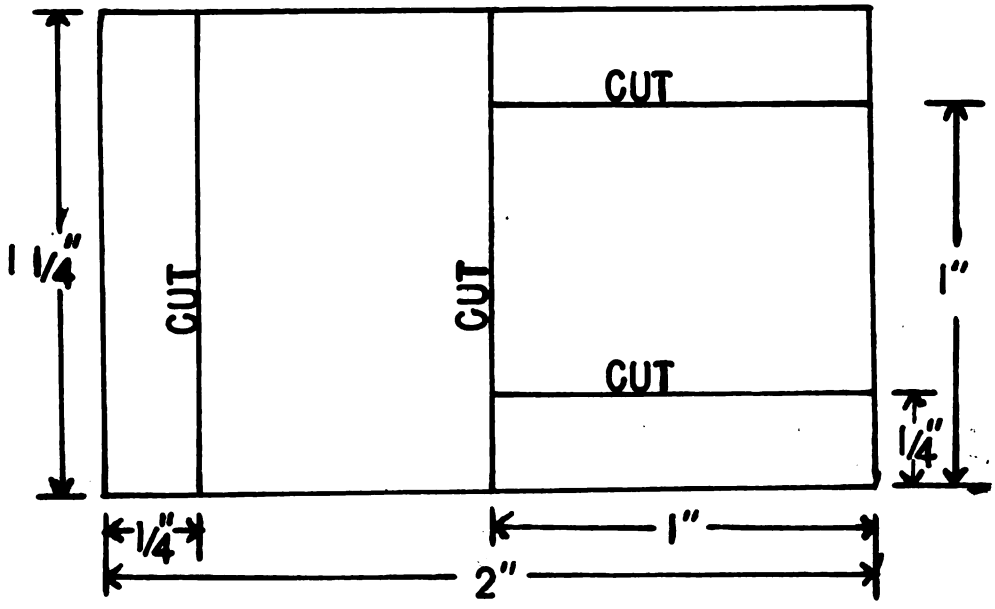
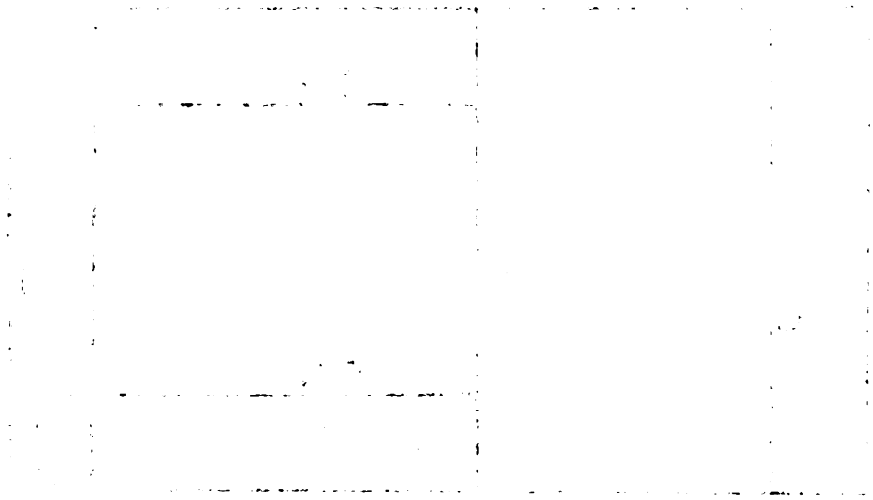


Figure No. 5 - Method of sectioning lip of bent cathode for thickness measurements.

The lips of the bent cathodes are cut off at the bend and sectioned as shown in Figure No. 5. The cut edges are mounted, polished, and etched as described later in this article under "throwing power and efficiency measurements". The specimens are measured for thickness of nickel deposit on a Bausch and Lomb Research Metallographic microscope. The thickness values are converted to current densities and plotted to give Figures No. 6, 7, 8 and 9.



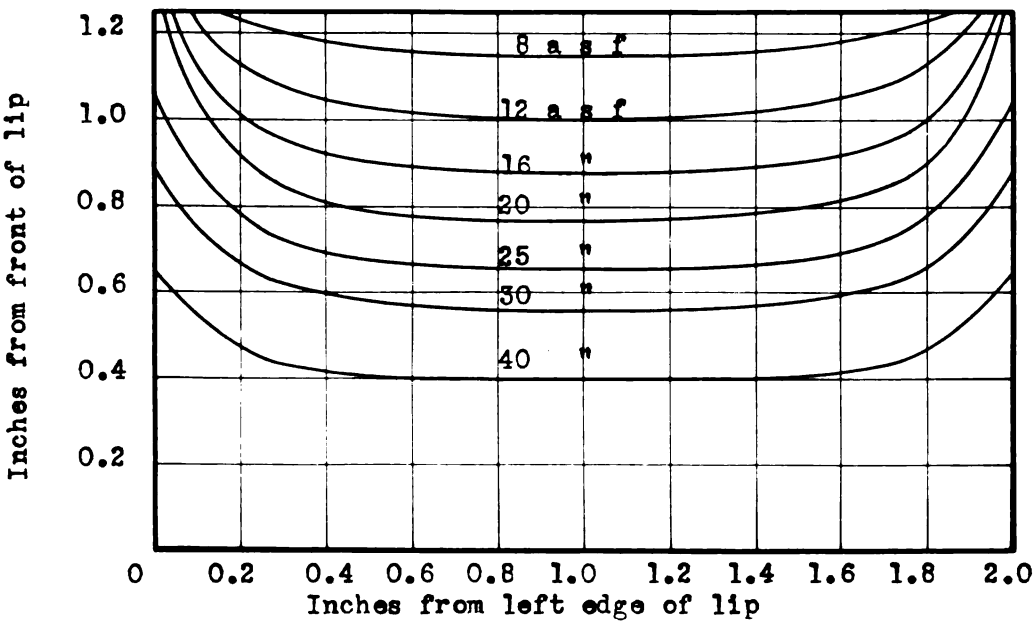


Figure No. 6 - Current density distribution on lip of bent cathode from Watts 2.2 pH solution

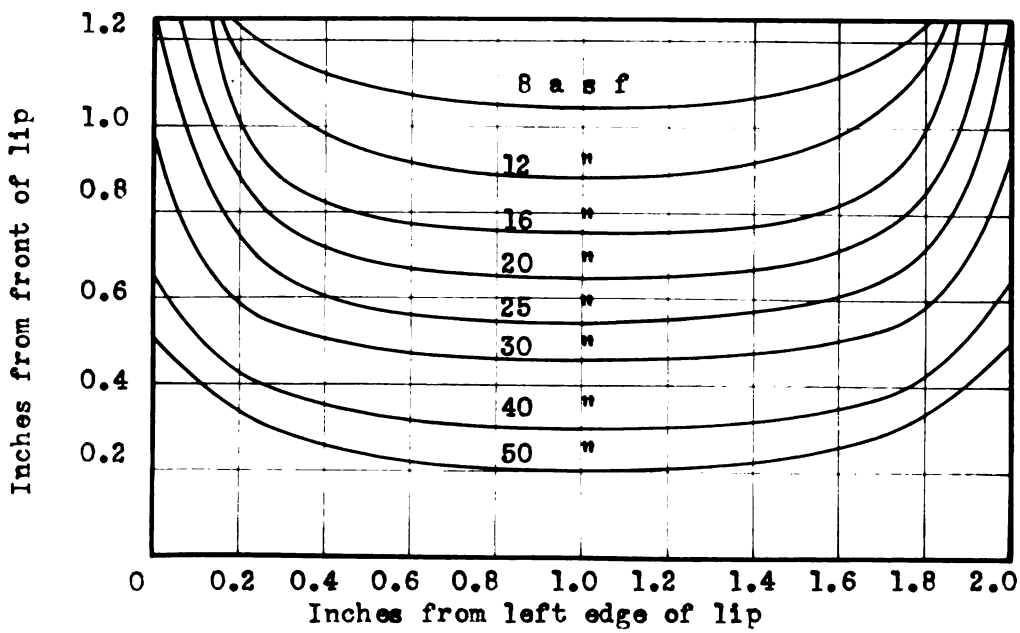


Figure No. 7 - Current density distribution on lip of bent cathode from Watts 5.2 pH solution

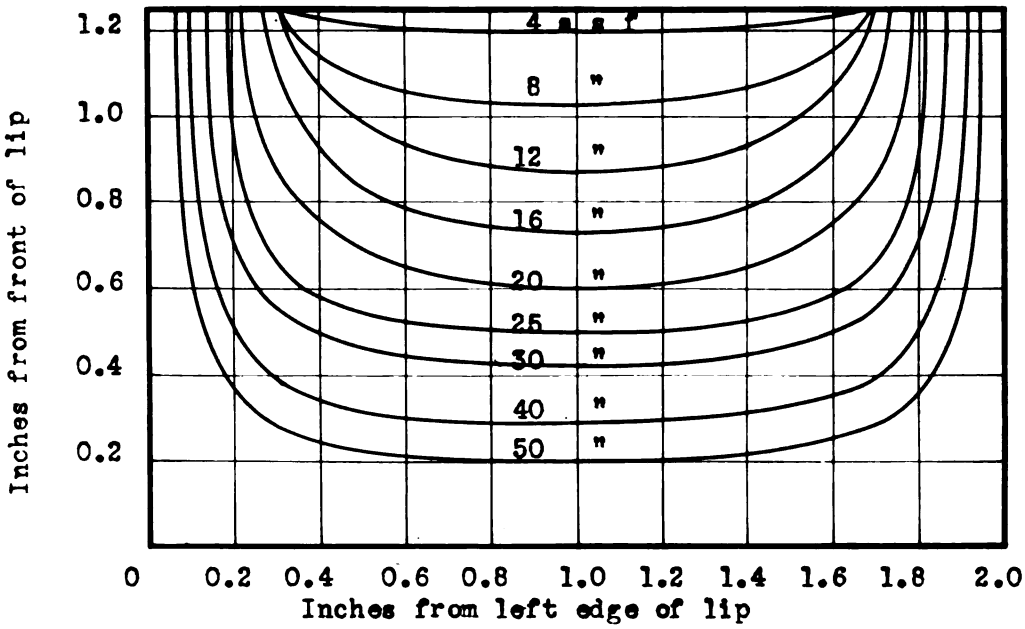


Figure No. 8 - Current density distribution on lip of bent cathode from Ni-Co Alloy-type solution

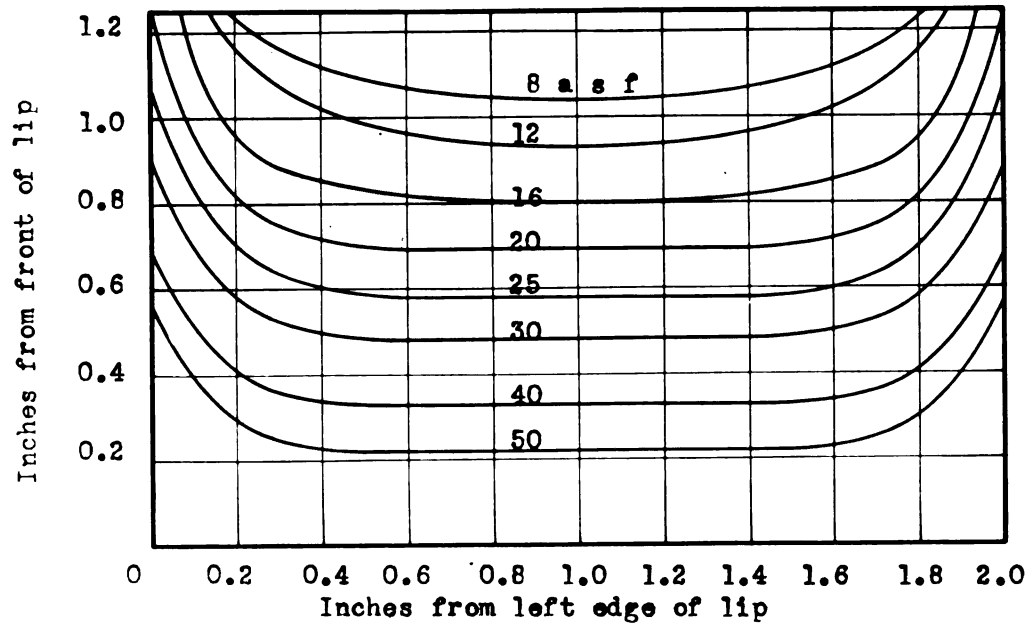


Figure No. 9 - Current density distribution on lip of bent cathode from Organic-type solution

Appearance

A 0.001" thickness panel is prepared from each of the pure plating solutions and for each concentration of impurity under observation. The Watts type grey nickel deposits are compared with the Eastman grey scale and assigned a scale rating, while the bright nickel panels are assigned luster values ranging from a mirror bright to a dull matte deposit. These values and scale ratings are then reported as the appearance of that deposit. Roughness and pitting are noted.

Adherence

The lip of the 0.001" thickness bent cathode used in the appearance test is clipped off at the bend and the treed portion of the lip is cut off. The lip-section is bent 180° around a 3/16" mandrel along the middle of the piece and across the short dimension. The deposit is observed along the bend with a magnifying glass. Bending in this manner allows observation of the test at a range of deposit thicknesses. The non-adherence, deposit thickness and the current density at which there is non-adherence is reported. This latter information may be read directly from the equi-current density curves as above.

Salt spray corrosion resistance

Cathodes are prepared in triplicate with deposits of 0.0003" 0.001" and 0.0015" thickness for each pure solution and each concentration of impurity, this enables observation of the effect of impurity upon increasing deposit thickness. The lip of the cathode and

the upper unplated portion of the panel is cut off. The plated panels are then tested for corrosion resistance in a commercial type salt spray (fog) cabinet. The conditions followed are as described in the A.S.T.M. Standards, (A.S.T.M. Standards, Part 1-B, Non-ferrous metals, Page 773, 1946).

The breakdown is recorded after a condition is reached comparable to that of a set of standards previously prepared as a standard breakdown point. This set of standards showed conditions before, at, and after breakdown points had been reached. This breakdown point was arbitrarily selected upon examination of prepared test panels after the salt spray corrosion test. After project committee approval, the standards were lacquered for permanent reference. The corrosion resistance is reported as a percentage change in resistance from the resistance of deposits from pure solutions.

Ductility

It has been found that a nickel deposit on steel is not sensitive enough for a ductility test and hence it was decided to use a stripped deposit for testing. This deposit is produced by first preparing a bent cathode with a deposit thickness of approximately 0.0003" on the vertical portion. Using this cathode, the previously described cleaning cycle is repeated using 15 second periods instead of the 2 minute periods. The cathode is immediately replaced in the plating solution and a deposit of 0.001" thickness is plated on the prepared surface.

If correct procedure has been used, the deposit will cover the prepared surface completely but may still be readily pulled from the surface.

A piece of the stripped deposit 1"x2" is creased between the fingers across the short dimension. Creasing and straightening, alternately, between the fingers until rupture occurs. A check determination is run and the results averaged. The average number of bends necessary to produce rupture is recorded and the results reported as an increase, decrease or no change in ductility in relation to the pure deposit.

Hardness

The vertical portion of bent cathodes deposited to a thickness of 0.002" are tested for hardness on a Knoop Hardness tester by Dr. William Blum, Director of Electrochemical Division, National Bureau of Standards, Washington, D. C. Results are reported as a percentage change in hardness from the pure deposit.

Throwing power and efficiency

Bent cathodes of 0.002" thickness are prepared from each of the pure solutions and for each concentration of impurity under investigation, and the lips of these cathodes are cut off. The equi-current density curves previously described showed that these lips could be used as a measurement of the throwing power and efficiency of the solution. A microscopic thickness test is made on each series and is

compared with the deposit from the corresponding pure bath. Differences are reported as the net change in efficiency and throwing power. If no change in gassing is noted, the change in thickness may be assumed to be due to a difference in throwing power.

The lip previously cut from the cathode is then carefully cut in half across the short dimension. The pieces cut off in this manner are placed, with the cut portion down, in a clamp made from two pieces of steel 1 3/4"x1"x$\frac{1}{4}$", and held together with two machine screws. Two pieces of sheet tin can stock one inch square, are placed between each piece to be measured and the clamp tightened. The samples are polished successively on coarse, medium, and fine emery papers, followed by polishing wheels with 320 and 500 mesh emery and fine alumina. The samples are then etched with "nital" (5% nitric acid in ethyl alcohol) for 20 seconds to bring out the contrast between the nickel deposit and the steel.

The polished and etched sample is placed on the stage of a Bausch and Lomb Research Metallographic microscope. On the standard deposit from the pure bath, the difference in drum readings is recorded from the front edge of the steel to the point on the top side of the lip where the deposit is 0.002"thick. On each succeeding panel the same distance is measured from the front edge of the steel and the micrometer readings of the thickness of the deposit on the top of the lip are recorded. The micrometer readings are converted to inches and the percent change in throwing power and efficiency is calculated as follows:

Percent of change in throwing power and efficiency =

$$\frac{0.002" - \text{thickness at point of unknown}}{0.002"} \times 100$$

The loss or gain in throwing power and efficiency is reported as the percentage change from the standard deposit from the pure solution.