THE EFFECTS OF IMPURITIES ON ELECTRODEPOSITED NICKEL WITH SPECIAL REFERENCE TO CALCIUM

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ABSTRACT

Four different types of buffered nickel sulfate plating solutions were investigated with respect to the quality of deposit produced when contaminated with various metallic impurities. The physical properties investigated were: appearance, adhesion, ductility, hardness, throwing power, and corrosion resistance. Calcium when present as an impurity in an amount less than the solubility limit had negligible effect on the above properties. Methods studied for the removal of calcium from these solutions included high pH precipitation, electrolytic removal, high temperature precipitation, and a precipitation with hydrofluoric acid. The roughness produced by copper impurity was investigated by metallographic techniques, chemical analysis, current density variations, base metal changes and polarization considerations.

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INTRODUCTION

The metal nickel possesses a fortunate combination of physical and chemical properties which have established it as one of the most important metallic coatings used for protective and decorative purposes. It exhibits relatively high strength, ductility and hardness while at the same time displaying a high resistance to corrosion. The favorable properties of nickel together with the development of coating techniques have lead to a marked increase in the use of nickel coatings in recent years. This is particularly true of the electroplating industry which experienced wide expansion following the development of "bright nickel" plating. A further advantage is the close control and wide range of thickness that can be obtained.

The principal limitation of nickel as a coating metal lies in its electropositive relationship toward iron in most environments. Deposit discontinuities are highly undesirable in the case of cathodic coatings of this type where exposed base metal becomes anodic and dissolves away. In fact the base metal which is exposed through discontinuities in a cathodic coating can deteriorate at a much faster rate than if the coating were not present at all. This is because of the localized electrochemical cell which is set up in the presence of corrosive electrolytes. Therefore, cathodic coatings must be as continuous as possible to obtain a maximum in corrosion protection.

The complexity of present day nickel plating baths as well as the variety of uses to which electrodeposited nickel is applied has prompted

extensive research concerning the variations in the physical and mechanical properties of the nickel brought about by changes in bath composition, temperature, pH, current density, and level of impurities. The detrimental effects of certain metallic impurities has long been known; however, previous to this research project no systematic study of the effects of individual impurities as well as of combinations of these impurities has been undertaken. Impurities find their way into nickel plating baths in a number of ways of which "drag in", impure nickel salts and a contaminated water supply are the chief contributors.

Sponsored by a fellowship grant from the American Electroplaters Society a series of metallic impurities was investigated with respect to their individual affect upon the appearance, adhesion, ductility, hardness, throwing power, and corrosion resistance of the electrodeposited nickel. These properties are particularly affected when the impurity either co-deposits or is occluded in some manner in the nickel deposit. The results of these investigations were reported merely on a relative basis, that is, the deposits from solutions of controlled impurity were compared with deposits obtained from a highly purified bath and any variations in a certain property were noted. Some very surprising phenomena in regard to the behavior of different metals electrodepositing simultaneously were revealed in these studies. It would normally be expected that two metals as similar to each other as nickel and copper being completely soluble in all proportions, having the same crystal habit, nearly the same lattice constants, and the same valence, would be deposited together with little or no interferences. Such was not the case, however, as the nickel deposits

containing trace amounts of copper were rough, black, and completely unacceptable from a corrosion resistance standpoint. On the other hand lead, an element far removed from nickel in the periodic listing of the elements and whose lattice constants vary considerably from those of nickel, provides a general brightening effect on both the Watt's type and bright nickel deposits. Also zinc, which crystallizes in the hexagonal lattice system, when added to the nickel baths as an impurity produced a slightly brighter deposit whose corrosion resistance showed a general increase with increasing concentrations of zinc. Other elements investigated such as aluminum, iron, manganese, and chromium although differing from nickel to varying degrees produced no significant changes in the nickel deposit. Since no attempt was made in any of the previous reports on impurity studies to explain these rather unexpected results it was undertaken to search for further evidences of these peculiarities and thereby to be able to clarify and explain the actual mechanisms involved. It was decided to carry out a thorough investigation of the element calcium which is known to be present in nickel plating baths and is known to have adverse affects on the electrodeposit under certain conditions. The principal source of calcium in a nickel plating bath is the use of hard water in the make-up of the bath.

In spite of the common occurence of calcium as an impurity in plating solutions, very little work has been performed in investigating its effects. A comprehensive review of the literature has revealed that the only case of an intentional addition of calcium to a nickel plating bath dates back to 1916. In that year B. E. Miller (1)

advocated the use of calcium chloride as a conducting salt. It was subsequently shown that the action of the calcium chloride was to precipitate calcium sulfate, thereby replacing the sulfate ions with chloride ions. To accomplish this same end more directly Robins (2) advised the use of nickel chloride. No further reference to calcium appeared until 1939 when Meyer (3) pointed out that through the use of hard water rough deposits resulted due to the suspended calcium sulfate. About this same period Hogaboom (4) also reported on the detrimental effects of hard water on the nickel deposit. In 1941 Diggin (5) reported the results of his investigations on the effect of various water impurities on nickel deposits. He found that calcium itself appeared to have little effect, but the formation of calcium sulfate caused bright nickel to plate dull and spotted. These conclusions were corroborated by further work by Diggin (6) and also by Kushner (7) who studied impurity build up from drag-in of rinse water. Since that time little further has appeared on this subject.

Any possible existing correlation between the surface roughness caused by calcium and that caused by copper was investigated with special emphasis being placed on the mechanism of formation of the irregularities produced by copper. The report on the effects of copper impurity on electrodeposited nickel (8) indicates that amounts of copper in excess of 50 mg/l produce a deposit which tends to be rough and dark. Also shown is the drastic drop in corrosion resistance with the addition of trace amounts of copper. As far back as 1911 (9) a definite darkening of the electrodeposit was observed when copper was added in small amounts to the nickel solution. Some time later investigations carried out at the National Bureau of Standards (10) (11) again revealed the detrimental effect of copper which produced a dark, spongy deposit. These results were later confirmed by Eckelmann(12), Johnson (13), and Francis-Carter (14). Up to the present time the reason for this type of deposit has not been explained. The exploratory procedures utilized in this investigation for the purpose of discovering the actual physical phenomenon responsible for this undesirable electrodeposit include: a cross-sectioning of the spongy deposit which made it possible to take photomicrographs of the structure; spectographic analysis of the spongy nodules and of the foil; current density tests utilizing the Hull cell; voltage versus amperage characteristics at various copper levels; and buffing and plating experiments.

This work was supported by the American Electroplaters' Society by means of a fellowship grant, and the author is deeply indebted to this society for this necessary financial assistance. Also the technical and experimental assistance received from the project committee; Mr. C. Nixon, Mr. L. Borchert, and Mr. L. Morse is greatly appreciated. Finally my most sincere thanks to Dr. A. J. Smith for his invaluable guidance and encouragement throughout this work.

EXPERIMENTAL

In this study nickel deposits were prepared from four different types of plating bath (Table I). The Watts'-type nickel plating solutions (at pH 2.2 and 5.2) were employed to produce dull nickel deposits. The bright nickel deposits were obtained from a nickel-cobalt alloy type bath (pH 3.75) and from an organic type solution (pH 3.2) containing nickel benzene-disulfonate and triaminotolyl-diphenylmethane. Very small amounts of an antipitting agent in the form of sodium lauryl sulfate were added to all but the nickel-cobalt bath. The methods of preparation and purification of these solutions are outlined in detail in an article resulting from early work on this project (15). It was first attempted to determine the approximate solubility of calcium at normal plating temperatures. Calcium was added as calcium carbonate in considerable excess. After equilibrium had been reached at the proper pH, and settling was completed, the clear solutions were withdrawn and analyzed. The following appears to be the limit of calcium solubility in the respective solutions.

Watts'	2.2 pH	1000 + ppm
Watts'	5.2 pH	700 ppm
Organic	3.2 pH	1000 + ppm
Nickel-Cobalt	3.75 pH	1000 + ppm

It was determined (16) that on an average, commercial plating baths contained a maximum calcium content of 700-750 ppm, while the average concentration was approximately 350 ppm. With these figures as a guide, and since the consensus of opinion was that the calcium ion was relatively harmless it was decided to limit the experiments to three levels of calcium concentration; a pure bath (0 ppm Ca), an average calcium level (350 ppm Ca), and a level corresponding to the upper limit found in normal plating solutions (700 ppm Ca). The calcium was added in the form of calcium carbonate so as not to alter the sulfate-chloride ratio of the individual baths. Following these additions the pH was adjusted back to the normal operating range with sulfuric acid. Panels of four different thicknesses were plated from each bath and at each level of calcium concentration. The actual plating process, including the cleaning of the panels, has been described in detail in earlier publications from this project (17) (18) (19). The thicknesses were chosen with regard to the ultimate tests to be run.

The evaluation of the deposits obtained was accomplished by a quantitative comparison of the deposits from solutions containing varying amounts of calcium with panels produced from pure solutions. Deviations were reported as percent change from the properties of the pure deposit, since in this case trends were the objective instead of absolute data.

The analytical method originally employed for the determination of calcium was the colorimetric procedure outlined by Serfass (20) in which the nickel is separated from the calcium in the form of a nickel hydroxide precipitate. The calcium is then precipitated as the oxalate which is filtered and then dissolved in sulfuric acid. The color is subsequently developed by the addition of a standard potassium permanganate solution, the degree of color being proportional to the amount of calcium oxalate present. The colorimeter readings are then referred

TABLE I

NICKEL PLATING SOLUTIONS

	Watts' Type	Organic	Nickel-Cobalt
Nickel Sulfate	240 g/l	262 g/l	240 g/l
Nickel Chloride	45	60	45
Boric Acid	30	34	30
Nickel Formate			45
Cobalt Sulfate			15
Nickel Benzene Disulfonate		7.5	
Triaminotolyldiphenylmethane		0.14 ml/l	
Temperature °F	55	60	60
pH (electrometric)	2.2 and 5.2	3.2	3.75
Current density (amperes per square foot)	40	40	40

to a standard curve which reveals the calcium content. This procedure which involved several filtrations and the evaporation of a considerable amount of liquid proved to be very tedious and time consuming. Consequently it was endeavored to accomplish these determinations by a much more direct and equally reliable means; namely, a direct spectrographic determination of the calcium in a measured quantity of plating bath.

In setting up this spectrographic procedure the usual spectrographic carbons were not used for two reasons. First, it was determined that even the most highly purified type of carbons still contained a certain measureable amount of calcium and secondly, the bath aliquots when placed on the carbons tended to soak in nonuniformly, thus giving erratic results. Pure copper electrodes were selected and proved to be satisfactory. A simple machining operation on a lathe cleaned the surface and readied the electrodes for use. The procedure consisted of sampling the bath and by means of a micro pipette placing .025 ml. on the flat copper electrodes. By placing the electrodes with sample under an infra-red lamp the solution was dried in a matter of minutes.

The means of excitation chosen was the a.c. spark rather than the d.c. arc, due to its more uniform nature in energizing the entire surface of the electrode and also the fact that the excitation energy derived from the spark is more than adequate to excite the calcium and nickel atoms in question. The internal standard method was employed in order to correct for any variations in the time of exposure, plate emulsion characteristics, or developing conditions. It was decided to use a weak nickel line for this purpose rather than adding

an additional constituent with excitation characteristics similar to calcium. An example of this would be strontium; however, in this case an insoluble strontium sulfate precipitate would form rendering it useless. The exposure time was thirty seconds, a period which allowed the sample to be completely burned, but at the same time maintained a negligible level of background in the spectrum.

Standards were made up by taking five portions of a pure nickel plating bath and introducing calcium in amounts increasing from twenty to one thousand mg./l. The standard solutions were run along with every series of unknowns and from them a standard curve was plotted. The unknown microphotometer readings were then referred to this curve for the final analysis. The analysis of samples by both the colorimetric and the spectrographic procedures established that the spectrographic method resulted in an equal or greater degree of precision as well as being much more rapid. The instruments used for these investigations were a Hilger large littrow type spectrograph and a Jarrell-Ash Recording Microphotometer.

EFFECTS OF CALCIUM AS AN IMPURITY IN NICKEL PLATING SOLUTIONS

Appearance:

For the evaluation of appearance with increasing amounts of calcium in the bath, panels of three different thicknesses were plated; namely, .003, .0010, and .0015 inches. The steel panels themselves were bent so that a vertical and a horizontal surface was available for plating. The vertical section had an overall current density range of 40 amperes per square foot. The horizontal section possessed low, medium, and high current density areas ranging in value from 10 to approximately 60 amperes per square foot. A cathode of this type permitted an additional evaluation, that is the effect of current density on the appearance.

The actual evaluation was kept as uniform as possible by maintaining the same relative position of the diffuse light source, the illuminated panel and the line of sight of the observer. The gray deposits were compared with the Eastman Gray Scale, while the bright deposits were classified as ranging from dull to mirror bright. In each case any change in appearance was compared to the deposit produced from a pure solution.

Both the Watts' pH 2.2 and 5.2 baths were judged to have an Eastman Gray Scale reading of 1-2 and there was no change in scale reading with increasing calcium content. The roughness of the panel lips (horizontal section) increased slightly with increasing calcium content. The increased calcium levels produced no appreciable change

in grain size or treeing effect at the panel edges. No change was noted in the appearance of the organic or nickel-cobalt bright deposits with increasing calcium content with the exception of a slight increase in roughness at the higher calcium levels. These panels were all rated as mirror-bright.

Adhesion:

In a general sense the adhesion of electrodeposited coatings to their base metal depends primarily upon their intimate contact. Consequently the presence of oxides, greases, or other extraneous material will naturally reduce the adhesion. Special care was exercised in cleaning the steel panels in order to maintain as nearly as possible a uniform, impurity free surface. The cleaning procedure is outlined in an earlier report from this project (15).

To test the affect of calcium on the adhesion of the nickel plated foil to the base metal a bend test was selected, since in this case the plated specimens were easily bent and destruction of the panels was not a consideration. The test consisted of bending the lip of the cathode, upper side outwards, 180 degrees around a 3/16 inch mandrel in the middle and across the short dimension (21). For this test only the lips from the 0.001 inch series of panels were used. The bend was examined under a microscope at 20 diameters for any evidence of cracking or flaking as well as any correlation between this property and the thickness of the nickel deposit as revealed from the front to the back of the lip surface. In this study, at all concentrations used, the calcium did not discernibly affect the adhesion of any deposit to the base metal.

Ductility:

Deposits of .001 inch thickness were made from the four baths at the designated calcium concentration levels. These deposits were made upon a passivated nickel surface so that they could be stripped in the form of a nickel foil. The ductility test which was then carried out on this foil consisted of repeatedly bending, creasing and then flattening out the deposit across a predesignated area with the fingers until a break was noted. The number of times that the foil can be creased and opened before fracture is a measure of ductility. The fact that the number of bends possible with these nickel foils is small places a definite limitation on the reliability of the data. To help minimize any human error each foil was sectioned and given to several individuals to test. The results of the tests are compiled in Table II and are reported as percent change from the ductility value of the pure deposits. The Watts' 2.2 bath showed no appreciable change in ductility over the entire range of calcium impurity. The Watts' 5.2 bath while exhibiting the identical degree of ductility as the Watts' 2.2 bath at a zero calcium level showed a gradual decrease in ductility with increasing calcium content.

The foils from the pure organic bath exhibited a much lower degree of ductility than the foils from either of the pure Watts' baths, but the addition of calcium to the bath had little effect on the ductility. The foils from the NiCo bath were by far the least ductile of all the experimental foils. In this case the ductility was so low that the test was rendered inaccurate; however, there appeared to be no significant change in the ductility with increased amounts of calcium.

TABLE II

EFFECT OF CALCIUM ON THE DUCTILITY OF ELECTRODEPOSITED NICKEL

Calcium concentration mg/l	Percent Change			
	Watts' pH 2.2	Watts' pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	0	0	0	0
350	0	-37	-16	50
700	9	-45.7	-12	50

Hardness:

Electrodeposited nickel may be obtained in hardnesses over a range of about 500 Brinell. These differences in hardness depend upon composition and structure and are obtained by adjustment of bath composition and plating conditions.

To obtain a true indication of hardness, consideration must be given to the thickness of the nickel deposit to insure against the effect of a comparatively soft base metal. In order to eliminate this error as much as possible a relatively thick nickel deposit (.002 in.) was plated from each of the baths. In this way the influence of the base metal was diminished and at the same time the deposit thickness was not so large as to alter the properties. Several instruments have been developed for measuring hardness of relatively thin deposits by virtue of their ability to employ light loads and measure accurately the degree of impression. These instruments measure the length of indentation or depth of penetration of a diamond tip under various degrees of pressure. The hardness measurements for this project were carried out by the National Bureau of Standards with a Tukon hardness tester employing Knoop type of diamond indentor.

The results which are tabulated in Table III reveal only slight changes in hardness with increasing calcium in the baths. Although the Watts' 2.2 bath shows a slight increase and the Organic bath a slight decrease in hardness the changes are not significant and no definite trend is established. As expected the bright deposits show a much higher hardness than the Watts' dull nickel, with the NiCo deposits possessing the highest hardness.

TABLE III

EFFECT OF CALCIUM ON HARDNESS OF ELECTRODEPOSITED NICKEL

Calcium concentration mg/l	Percent Change			
	Watts' pH 2.2	Watts' pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	0	0	0	0
350	1.6	5.5	-5.1	-6.1
700	10.1	-11.7	-7.6	3.0

Throwing Power:

It is usually desirable that the deposited metal be distributed uniformly over the surface to be covered even though this surface may be very irregular. In order to accomplish this purpose, solutions of rather complex composition are often employed that are particularly effective in depositing the metal in recessed areas, thus exhibiting what is known as high "throwing-power".

Throwing power was evaluated by a procedure outlined in an earlier paper from this project (15). The method consists of sectioning the horizontal lip of the bent cathodes which were plated to a thickness of .002 in and after clamping, polishing, and etching, the thickness of the electrodeposited nickel relative to the pure deposit was measured by means of a Bausch and Lomb research metallographic microscope. As described in another project paper, the throwing power measurements were performed on both the top and bottom of the lip to minimize the variation in the results due to a non-horizontal cathode lip during the plating (22). The distribution of electrodeposited metal depends on the distribution of current and the respective cathode efficiencies at the prevailing current densities. Since no gassing was noted in the concentration ranges studied as long as plating conditions were controlled, the efficiency was assumed to be unchanged. Therefore, any change in the deposit thickness was assumed to be due to a change in the throwing power of the solution.

The results of this test which are summarized in Table IV indicate an overall reduction in throwing power with increasing calcium content. However, the measurement itself involves an error of approximately 10

TABLE IV

EFFECT OF CALCIUM ON THE THROWING POWER OF ELECTRODEPOSITED NICKEL

Calcium concentration mg/l	Percent Change			
	Watts' pH 2.2	Watts' pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	0	0	0	0
350	-0.5	-1.0	-7.3	-4.8
700	-10.5	-5.0	-8.3	-2.3

per cent and so the variations are not considered significant and no clear cut trend is established.

Corrosion Resistance:

Undoubtedly the primary reason for the electrodeposition of one metal on another, other than decorative purposes, is to eliminate or at least hinder the destruction or deterioration of the metal by direct chemical or electrochemical reaction with its environment. To accomplish this protection of steel with electrodeposited nickel the coating must be continuous and completely cover the basis metal. In order to evaluate the protective qualities of nickel deposited in the presence of increasing amounts of calcium it was necessary to employ some form of accelerated corrosion test that would duplicate as nearly as possible normal service corrosion. Employed was the most widely used test at the present time, the salt spray (fog) test, the conditions of which are outlined in the A.S.T.M. Tentative Method of Salt Spray (fog) Testing B117-49T. This test which was designed as a comprehensive accelerated corrosion test has been the subject of a considerable amount of controversy and is now undergoing intensive efforts at standardization. Because of this almost universal skepticism concerning the results of the salt spray test it was deemed necessary to substantiate the results by employing other corrosion tests on similar test panels. The acetic acid modification of the salt spray which incorporates a lower operating temperature and a lower salt concentration was employed. Also used was a recently developed electrochemical test developed by Pierce and Pinner (23) in which the nickel coating is the anode and a copper wire the cathode in a cell which utilizes sodium chloride as the electrolyte.

Triplicate panels of 0.0010 inch thickness were prepared from each solution to be tested. These were placed in the salt spray (fog) cabinet and allowed to remain until breakdown was judged to be complete. Although there was an obvious difference between the corrosion resistance of the bright and dull deposits, the bright deposits lasting twice as long as the dull deposits, there was no indication as to the effect of increasing calcium content on corrosion resistance of the nickel. The period of time required for failure of the panels varied greatly within each level of calcium concentration, thus making it impossible to establish any kind of trend. The type of corrosion encountered nearly always involved three or four spots which gradually grew until the panel had failed. These spots were very likely strongly anodic and were protecting the remaining nickel surface. In a few instances the panels developed more of an overall corrosion pattern with a large number of rust spots appearing. This type of corrosion would tend to indicate a more porous nickel structure. In cases where the panels lasted for 120 hours the corrosion seemed to come to a standstill and further cabinet time would have been futile. The water insoluble gray film mentioned in previous papers (22) was evident and perhaps was the protective agent preventing further corrosion.

Through the cooperation of the General Motors Research Laboratory it was possible to test a series of panels in their acetic acid salt spray chamber. For these tests a series of twelve panels of 0.0010 inch thickness were plated from each of the test solutions. The tests were carried out under the direction of Mr. C. F. Nixon according to the specifications outlined in A.S.T.M. B287-54T which essentially call for a 5 percent sodium chloride solution, pH 3.4 with acetic acid, at 35°C. The panels were exposed for eight 24-hour periods and following each period the panels were rinsed with cold running water and inspected. A rating number was assigned to each panel at each interval and the findings were reported in terms of Performance Index numbers.

The rating scheme was as follows:

Amount of Failure	Rating
None ------ no failure	5
Slight ---- 1 to 10% of significant surface affected	4
Moderate -- 10 to 30% of significant surface affected	3
Severe ---- 30 to 70% of significant surface affected	2
Total ----- over 70% of significant surface affected	1

The Performance Index Number was based on these ratings for each of the eight inspections, as shown in an example below.

Hours	24	48	72	96	120	144	168	192
Rating	5	4	4	4	3	3	2	1

The sum of the ratings (26) is multiplied by an arbitrary constant 2.5. The product is by definition the Performance Index Number. The possible values range from a minimum of 20 to a maximum of 100. Number 20 represents a part which has totally failed in 24 hours and number 100, a part which shows no evidence of corrosion at the conclusion of 192 hours of testing.

The results are tabulated in Table VI and each value represents the average of twelve Performance Index Numbers. Here the results of the Salt Spray Test are substantiated in that there is revealed no

TABLE V

EFFECT OF CALCIUM ON THE CORROSION RESISTANCE OF ELECTRODEPOSITED NICKEL AS DETERMINED BY THE SALT SPRAY (FOG) TEST

	Average Number of Hours to Produce Failure			
Calcium concentration mg/l	Watts' pH 2.2	Watts' pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	41	55	103	113
350	72	48	79	103
700	41	55	79	113

evidence of either an increase or decrease in corrosion resistance with increasing calcium in the plating bath. Again the NiCo bright deposit exhibited the greatest corrosion resistance.

As an additional check on the validity of these corrosion resistance results a third corrosion test was utilized, namely, the electrochemical method of Pierce and Pinner (23). This approach to the problem of finding a positive means for evaluating electrodeposits with respect to their corrosion resistance was based on some original work by Shome and Evans (24). These investigators developed a cell consisting of a copper electrode, a thinly nickel plated steel electrode and a sodium chloride electrolyte. The potential generated by the Shome and Evans cell was found to be approximately 0.2 volts. In the Pierce and Pinner corrosion cell which is described in detail in an earlier paper (25), the potential was increased to 0.3 volts by the addition of a battery powered potential source in order to increase the sensitivity when applied to thicker deposits.

Electrochemical corrosion tests were carried out on duplicate panels of 0.0003, 0.0010, and 0.0015 inch nickel thickness from each of the four plating baths and at each calcium concentration. The thin (0.0003 inch) deposit was tested for two hours, the 0.0010 inch deposit for three hours, and the heavy (0.0015 inch) deposit for four hours.

In Table VII the figures representing the number of corrosion spots are the average of both panels. The results here proved to be very erratic and no significant change in corrosion resistance was indicated.

TABLE VI

EFFECT OF CALCIUM ON THE CORROSION RESISTANCE OF ELECTRODEPOSITED NICKEL AS DETERMINED IN THE ACETIC ACID SALT SPRAY (FOG)

	Calcium Concentration mg/l	Performance Index		Standard Deviation
		Average	Range	
Watts' 2.2 pH	0	57.7	47.5-72.5	6.9
	350	56.3	50.0-62.5	4.5
	700	56.7	50.0-62.5	3.9
Watts' 5.2 pH	0	55.8	47.5-65.0	5.6
	350	57.5	42.5-65.0	6.5
	700	55.4	42.5-67.5	7.8
Organic 3.2 pH	0	53.8	45.0-65.0	5.5
	350	52.3	42.5-70.0	8.8
	700	55.6	42.5-62.5	5.7
NiCo 3.75 pH	0	59.2	50.0-65.0	4.4
	350	61.7	52.5-72.5	5.9
	700	63.1	55.0-72.0	4.9

TABLE VII

EFFECT OF CALCIUM ON THE ELECTROCHEMICAL CORROSION RESISTANCE OF ELECTRODEPOSITED NICKEL

	Calcium Concentration mg/l	Average Number of Corrosion Spots (2 hours) 0.0003 in.	(3 hours) 0.0010 in.	(4 hours) 0.0015 in.
Watts' 2.2 pH	0	7.5	7	3
	350	4	7.5	6
	700	8.5	11.5	11
Watts' 5.2 pH	0	6.5	4.5	3
	350	12	8.5	13
	700	10.5	19	7.5
Organic 3.2 pH	0	9	18	5.5
	350	5	13	5
	700	2.5	16	13
NiCo 3.75 pH	0	4.5	6.5	12
	350	2	9	9
	700	4	5.5	3.5

REMOVAL OF CALCIUM FROM NICKEL SOLUTIONS

The removal of calcium was attempted by several methods, including low current density electrolysis, high pH precipitation, high temperature removal, and a chemical procedure involving treatment with hydrofluoric acid. The procedures for both the electrolytic and high pH removal were described in a previous publication by Ewing, Rominski and King (15).

Standard operating conditions of pH, temperature, and rate of agitation were maintained in the study of the electrolytic removal of calcium. Also care was taken to use nickel plated cathodes since it had been shown in an earlier investigation that at low current densities the steel cathode was not covered quickly enough to prevent the dissolution of iron and subsequent contamination of the solution. The current densities investigated were 2, 5, 10, and 40 amperes per square foot for each of the four plating baths containing 600 mg/l of calcium. The solutions were sampled periodically and analyzed for the calcium content by means of the spectrographic method outlined earlier. The results indicated no removal of calcium at either the low current densities or at the operating level of 40 amperes per square foot. An additional check on these results was possible through a spectrographic analysis of the dummy cathodes used in the electrolysis. These electrodes revealed no calcium being deposited, thus agreeing with the analysis of the plating baths before and after electrolysis.

The removal of calcium by high pH precipitation was attempted by the addition of nickel carbonate to the baths containing 600 mg/l of calcium until the pH reached the 5.6-6.0 range. The baths were held at this pH for 72 hours with samples being taken periodically for spectrographic analysis. The results of these analyses indicated that no calcium was being removed by this treatment.

The effect of increasing temperature on the calcium level was investigated by sampling a Watts' plating bath containing 600 mg/l of calcium ion at temperatures ranging from 25 to 70 degrees centigrade. The bath was allowed to reach equilibrium at each temperature level before sampling. The results of spectrographic analysis revealed that this range of temperature had no effect on the concentration of calcium at this concentration level.

An unpublished procedure for calcium removal involving a precipitation of calcium fluoride with hydrofluoric acid was investigated. The method consisted of heating the contaminate nickel solution to a temperature of 170°F and in another container heating a dilute solution of hydrofluoric acid to the same temperature. The nickel solution was then transferred slowly and with stirring into the acid container. In theory calcium and magnesium fluorides should form at this point and the precipitate could be filtered off. Several concentrations of hydrofluoric acid were employed in these experiments but in no case did this technique result in the removal of calcium from the plating solution.

DEPOSIT ROUGHNESS AS A RESULT OF METALLIC IMPURITIES

Reviewing the entire study concerning the effects of metallic impurities on electrodeposited nickel which included investigations into the effects of copper, iron, zinc, chromium (+3 and +6), lead, aluminum, manganese, and calcium, it is observed that one of the most if not the most incompatible metal is copper. Copper when present in a nickel plating solution in an amount usually considered as a trace ruins the appearance of the nickel by producing a deposit which is rough and black (25). Also when calcium is present to an extent exceeding 500 mg/l a certain roughness is evident. Any correlation between these two rough deposits could most certainly aid in the explanation of the mode of formation of rough, undesirable deposits. A definite loss in ductility of the electrodeposited nickel is also detected when copper ions are present in the plating solution. In addition the detrimental effects of copper are made manifest in the commercially important physical property referred to as corrosion resistance. The nickel deposits showed a definite loss of corrosion resistance, a loss which increased with increasing copper content.

The question arises as to the reason underlying these detrimental effects of copper. Why should two metals which are completely soluble in one another in all proportions behave in such an illogical manner when they are both forced to plate out together from an electroplating bath? Examination of the crystalline habits of each metal reveals that they both exist with a face-centered cubic lattice. The a_o

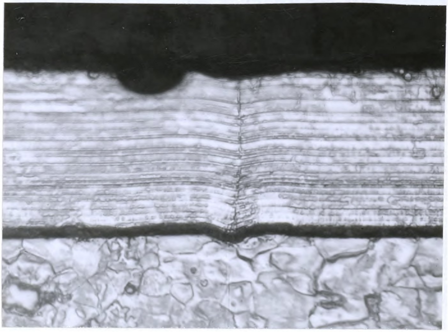
values for copper and nickel as reported in the A.S.M. Metals Handbook are 3.6080 and 3.5167 respectively and the closest approach of atoms is 2.551 for copper and 2.486 for nickel. The very close similarity of these two metals in regard to their crystalline structure almost certainly precludes the possibility of a lattice disturbance of any consequence.

Considering the decrease in corrosion resistance of electrodeposited nickel brought about by copper ions in the plating solution it may be well to first discuss the corrosion resistant properties of a pure nickel deposit. It is well known that electrodeposited nickel is limited in its corrosion protection properties by pores and imperfections in the plate due to several factors some of which are surface defects in the base metal, solids carried over in the plating bath, and the deposition of hydrogen gas along with the nickel. Thickness is the most important factor in controlling the porosity of nickel coatings. The number of pores per square decimeter below a deposit thickness of .0005 inches increases at an extremely rapid rate. The primary cause of this initial gross porosity in a nickel deposit is undoubtedly related to the hydrogen bubble formation which commences with the deposition of nickel. If these bubbles are not dislodged by the action of surface tension, agitation, or other disturbing factors, they will tend to grow at least as rapidly as the deposit and will prevent a closing up of the cavity. The result of this type of growth will be a pit which is visible at the surface. Figures I and II illustrate this type of fault in electrodeposited nickel.

With these facts in mind we may now consider the effects that copper may possibly have upon this mechanism. The first approach to the problem was a study of the cross-section of these deposits to determine the nature and mode of formation of the rough, spongy structure. Eighty milligrams per liter of copper in the form of $CuSO_4 \cdot 5H_2O$ was added to a nickel-cobalt bath which was known to be plating bright. Panels were plated from this impure bath under normal operating conditions with the periodic addition of copper solution in order to maintain the impurity level at 80 mg/l (25). These panels were sectioned perpendicular to their surface and mounted in bakelite molds to allow polishing and etching of the nickel structure. The etching was carried out in two steps (26) the first being for the purpose of removing the cold-worked surface. For this a mixture of one volume concentrated nitric acid, two volumes concentrated hydrochloric acid and two volumes glycerine was used. To reveal the grain structure, inclusions, and voids the surface was subsequently etched with a mixture of equal volumes of concentrated nitric acid and glacial acetic acid.

This roughness which develops as a result of copper impurity in the bath is apparently the result of a very unusual deposition phenomenon. Upon close examination this roughened surface is revealed to be a collection of individual nodules growing out perpendicular to the deposit surface. These nodules are seen to originate deep in the nickel deposit near the base metal if not actually at the base metal. As the deposition continues these nodules appear to grow at an ever increasing rate and the indication is that they become self propogating and branch out to an extent far exceeding any build up attributable to ordinary deposition. Illustrations of this unusual development are

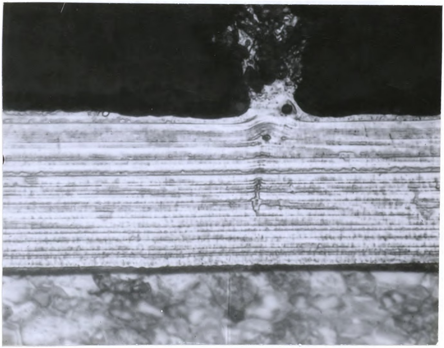
FIGURE I



A cross-sectioned nickel electrodeposit showing a cavity originating at the base metal and continuing through the nickel deposit.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

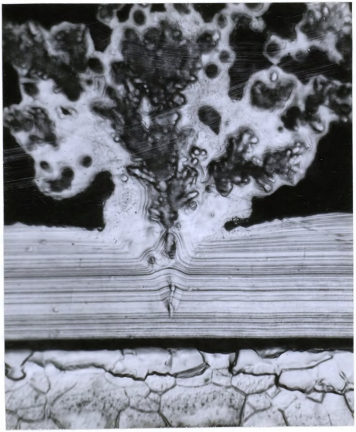
FIGURE II



A cavity in the nickel deposit which may or may not have originated at the base metal but which has continued through the nickel and has resulted in the formation of a nodule type imperfection.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

FIGURE III



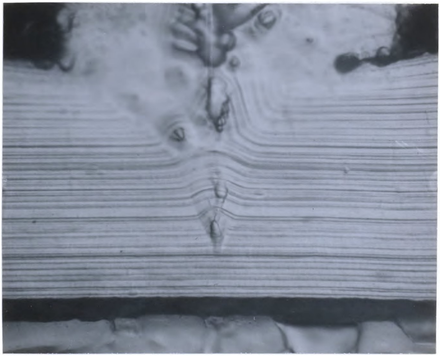
The cross-section of a typical nodular structure which illustrates the unusual growth phenomenon. Evident is the typical bright nickel striated structure and how it has been forced upwards into the nodule base.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

shown in Figures III through VI. Figure III reveals this unusual growth phenomenon and it is seen that the size of the nodule is far out of proportion to the deposited layer. The position of the true origin of this particular nodule is not really known. It is very possible that this particular plane of polish does not reveal a deeper imperfection running slightly back into the nickel. Likewise it is equally possible that the original growth pattern has already been polished away. The slight depression noted in the deposit surface directly under the nodule is believed to be due to a simple shielding action, that is, the deposit is shielded from the anode and a fresh supply of nickel ions. The characteristic bright nickel lamellar structure is seen to bend upwards into the nodule and is even noted well up inside the nodule. Figure IV represents the same growth area as in Figure III but at a higher magnification. It can be seen that as the nickel deposit is layed down an inclusion or obstruction of some sort has caused the normal banded structure to be bent upwards. This slight distortion is carried on through successive layers until at approximately three quarters the deposit thickness additional obstructions are encountered and the banded structure is forced to assume nearly a vertical direction. From this point on the growth of the nodule continues at a rate far greater than normal deposition. Figures V and VI are illustrations of similar nodule formation.

Figure VII was obtained by polishing a rough panel specimen in a direction parallel to the surface, thus in this picture we are looking directly down upon growing nodules which have been cross-sectioned

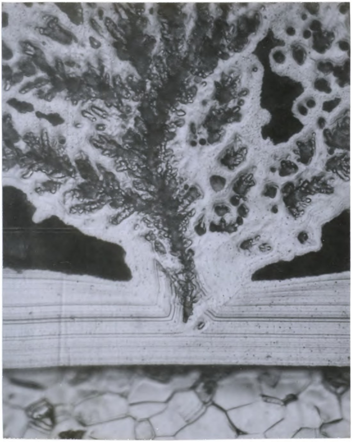
FIGURE IV



The same nodule growth as shown in Figure III but at a higher magnification. Clearly visible is the effect of an occluded mass in forcing the electrodeposit to bend upward and form a nodule.

Magnification: 1700X
Etchant: 1:1 conc. nitric acid and glacial
acetic acid.

FIGURE V



A cross-sectioned nodule in which the central core and the resulting vertical buildup of deposit are evident.

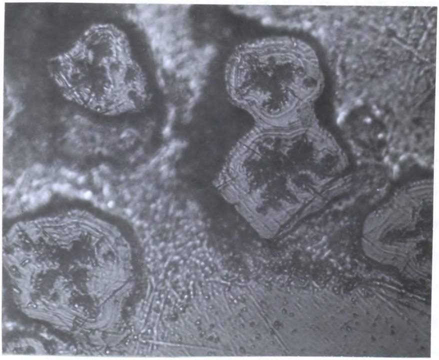
Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial
acetic acid.

FIGURE VI

A cross-sectioned nodule which has developed from several inclusion sites.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

FIGURE VII



A cross-section parallel to the deposit surface revealing the striated bright nickel structure extending up into the nodules.

Magnification: 1700X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

perpendicular to their principal growth direction. These polished nodules in the unetched condition revealed no holes or faults; however, the nodule sites were readily distinguishable by a difference in metallic luster. A very slight etch, one second in the 50% concentrated nitric acid - 50% glacial acetic acid revealed within the nodule areas voids or regions containing a material other than nickel immediately below the polished surface. These so called voids correspond to the dark areas shown in Figures III through VI.

An explanation of these nodules was sought by considering several different possibilities for their mode of formation. At the outset the phenomenon was believed to be a base metal problem. That is, imperfections in the steel panel whether pits, cracks, protrusions, impurities, or voids were given prime consideration as the possible sites of primary disturbance which eventually resulted in nodule formation. It was further postulated that these abnormalities were continued through the electrodeposited nickel and by a mechanism involving the copper ion the observed nodules developed. In an effort to substantiate or refute this theory by experimentation several investigations were undertaken in the laboratory. The first was designed to reduce or eliminate the effects of any base metal imperfections by initially depositing a smooth, bright nickel layer on a properly cleaned steel panel. Over this base layer then could be deposited an additional layer from a bath containing copper impurity and the degree of nodule formation noted. The first of these panels was made by plating a .0005 inch nickel deposit from a purified bright nickel bath and then without interrupting the plating, copper

sulfate solution was added to the bath to bring the copper impurity level up to 80 P.P.M. Following this addition another .0005 inch of nickel was deposited. Inspection of the final deposit revealed it to be rough and black with considerable nodule formation. Therefore although the steel was first coated with a smooth bright nickel deposit, the nodule formation resulting from copper ions in the bath was apparently unaffected. Repeated trials in which the deposit thickness and copper ion concentration was varied produced results of a similar nature. This would tend to contradict the theory that the nodules were originating at base metal imperfections.

Another investigation consisted of altering the base metal surface by buffing the steel panels on a cotton buffing wheel, the purpose being to smooth out the surface as much as possible and present to the nickel ions a comparatively level surface upon which to deposit. The technique used was to buff one half the panel surface and then note any variations between the buffed and unbuffed areas after plating. Repeated trials failed to reveal any discernible difference in regard to nodule formation between the areas which were buffed and those which were not. An interesting phenomenon which became evident in this investigation was that the position of the greatest concentration of nodules was dependent upon the direction of propeller agitation; that is, the nodules tended to concentrate along one side of the panel or the other depending upon the direction of bath rotation. It was invariably found that the side of the panel upon which the solution initially impinged as it traveled from the anode end of the rectangular tank, was the side possessing the majority of nodules. When the direction of propeller rotation was reversed the area of nodule concentration was likewise shifted to the opposite side of the panel. Other investigators have also noticed this relationship between solution movement and position of faulty deposit (10). This phenomenon of the dependence of the position of nodule concentration upon solution movement further refutes the base metal theory and strongly suggests that the underlying cause of this type of undesirable deposit lies in the solution and not with the base meta.

Further evidence to refute the theory of base metal originating nodules was obtained by polishing the surface of a rough, black deposit in a direction nearly parallel to the panel surface. Polishing in this manner afforded the opportunity of viewing the deposit over its entire range of thickness. The resulting microstructure after a suitable etch revealed a relatively pore free initial deposit continuing to a thickness of between .0002 and .0003 inches.

Although it cannot be said that nodules are not originating at deposit thicknesses of this order of magnitude or less, certainly there is little evidence of their formation when viewed at a magnification of 800X. Figure VIII is a photomicrograph of a portion of this tapered section at this magnification. It shows the bare steel and the gradual build up of nickel deposit to a thickness of approximately two tenthousandths of an inch. The granular nature of the nickel structure renders the detection of imperfections rather difficult; however, the uniformity of the surface would indicate the absence of any nodules at this stage of the deposition. Figures IX, X and XI are photomicrographs of this same tapered surface but at positions of

increasing deposit thickness. Figure IX represents a thickness ranging between .0003 and .0005 inch. At this point in the deposition nodules are very definitely forming and are very much in evidence at this magnification. The increasing number of nodule sites with increasing deposit thickness is very noticeable. In Figure X the size and number of the sites have increased considerably and the deposit, if the plating were ceased at this point would begin to take on a dark appearance. The deposit thickness in this photomicrograph increases from approximately .0006 to .0008 inch. In the final photomicrograph of the series, Figure XI, the deposit thickness has reached .0010 inch and the surface is almost completely covered with this abnormal form of deposit. The amount of metal removed by polishing from the particular portion of the surface in the lower half of the photograph was very slight, therefore the structure represents the basis of the rough, black deposits produced from copper contaminated nickel solutions. The conclusions that may be drawn from this series of photographs are that nodule formation does not necessarily originate at the base metal interface, and secondly that by means of some ever increasing reaction the frequency of nodule formation increases with deposit thickness. These photomicrographs, coupled with the results of the previous experiments already mentioned, indicate quite definitely that base metal imperfections have very little to do with the formation of these detrimental nodules. The origin of these unusual structural growths appear to be located at random throughout the deposit.

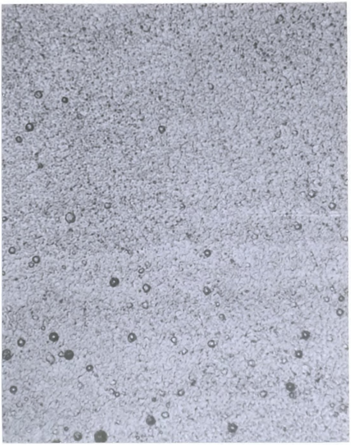
At this point in the investigation it became evident that an

FIGURE VIII

An electrodeposit polished nearly parallel to the deposit surface showing the steel base metal and the gradual build up of nickel to .0002 inch. Nodules are not apparent at this magnification.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

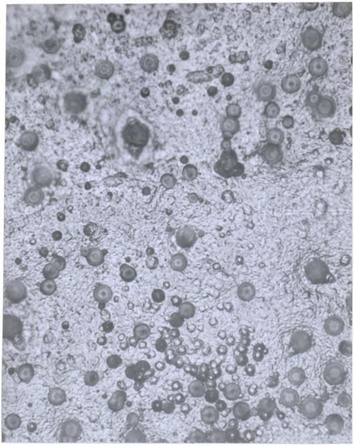
FIGURE IX



Electrodeposited nickel polished nearly parallel to the surface. The deposit thickness ranges from .0003 to .0005 inch with nodule formation evident at the thicker end.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial acetic acid.

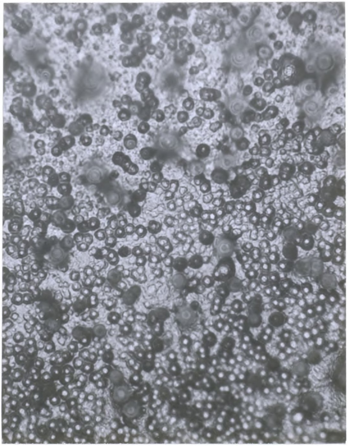
FIGURE X



Electrodeposit polished nearly parallel to the surface. The deposit thickness ranges from .0006 to .0008 inch from top to bottom.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial
acetic acid.

FIGURE XI



Electrodeposit polished nearly parallel to the surface. The deposit thickness increasing from .0008 to .0010 inch from top to bottom.

Magnification: 800X
Etchant: 1:1 conc. nitric acid and glacial
acetic acid.

understanding of the true mechanism involved in nodule formation would necessitate the evaluation of a number of different aspects of the plating operation. These factors would include first of all the chemical analysis of the nodular structure compared with the analysis of the smooth, bright nickel deposit in order to determine any possible compositiondifferences. Other influencing factors which warranted investigation were the effects of current density changes, polarization effects, and cathode film relationships. Such plating parameters as solution temperature, ionic concentration, and pH were held constant during these investigations; however, preliminary tests had previously indicated that moderate fluctuations of these factors had very little if any effect on the so-called nodule formation.

Composition differences between the smooth, bright deposit and the rough black areas could be very informative regarding the mechanism of formation of the rough deposits. Therefore it was undertaken to prepare a series of these black, rough deposits over a passivated film layer so that the deposit could be stripped and divided according to quality of deposit. It will be remembered here that the black areas were not uniform over the deposit surface but tended to concentrate on one side or the other depending on the direction of solution movement. This then afforded the opportunity of obtaining from a single deposit a normal smooth deposit area and an area of black nodules for analysis. The nodules were scraped from the surface so as to isolate them from the normal type of deposit and thus afford a means of analyzing them separately. The strip deposits were prepared in a manner much the same as the deposits used

for ductility measurements. A .0003 inch, bright deposit was obtained from a purified bath and this surface was passivated by a fifteen second alkaline cleaning operation followed by a fifteen second acid dip in 20% hydrochloric acid. The panel was then placed in a nickel bath containing 80 mg/l copper ions and a deposit .0010 inch in thickness was produced which was readily removable from the passivated surface. The black nodules were scraped from the surface to separate them from the smooth deposit areas. These two sample types, the nodules and the smooth bright nickel, were then analyzed by the very sensitive colorimetric method described by Serfass and Levine (27). According to this procedure, after the dissolution of a weighed amount of metallic sample, the copper is isolated from the other constituents by precipitation with 2 - Mercaptobenzothiazole and extraction of the precipitate with amyl acetate. The color is developed by addition of dibutyl amine and carbon disulfide. After the solution has been diluted to 25 ml. with ethyl alcohol its transmittancy is measured and this value compared to a standard curve to determine the milligrams of copper present. The results of these determinations are summarized in Table VIII.

The values presented in Table VIII represent relative amounts of copper in the normal smooth foil and in the nodules. These milligram values are not significant in themselves but only the comparison between the two. Considering the lowest foil value and the highest nodule figure, there is revealed a moderate increase in copper content in the nodules. This figure, however, only points out the possible concentration extremes. A more reasonable comparison would be

TABLE VIII

RELATIVE AMOUNTS OF COPPER IN SMOOTH FOIL AND IN NODULES

Sample	Mg Copper	Average (MgCu)
Smooth Foil	.0054	
" "	.0049	.0048
" "	.0037	
" "	.0053	
Nodules	.0058	
"	.0058	.0059
"	.0060	

between the two averages, and in this case the increase in copper content in the nodules amounts to about 18%. The indication here is that there is a slight concentrating effect on the copper ions in the nodules. This effect, however, is not pronounced and it would be erroneous to draw any definite conclusions on this basis along. If, however, other experimental data point to a probable concentration of copper in the nodules these results would offer definite support.

Considering now the various factors affecting plating operations it is noted that the character of the deposit obtained from a bright nickel bath depends upon a number of factors namely current density, temperature, pH, concentration of brighteners, concentration of additives, impurities, and others. Fortunately the variables affecting deposition are not all independent and the effect of nearly all the above factors will vary with the current density. Because of this dependence upon current density, more information as to the extent and kind of difficulty encountered can be obtained if deposits are made at a number of current densities. A convenient means of achieving this with a single plate is afforded by a device known as the Hull Cell. This is a plating cell which has the cathode inclined with respect to the anode with a resultant variation of current density with distance along the plate. With this means of evaluation then it was decided to determine the effect of current density upon nodule formation from a bright nickel plating solution containing copper ions as an impurity. The Hull Cell was cleaned and arranged in a water bath so that the normal operating temperature could be maintained. The impure plating bath was prepared in standard plating tanks and

agitated until completely homogeneous. From this solution was withdrawn the cell samples and the plating was carried out using steel panels which had been cleaned in the usual manner. The results of these tests although not producing any clear cut evidence of either high or low current density requirements for nodule formation did tend to indicate that at higher current densities the nodule growth was favored. This was evidenced by the fact that the concentration of nodules was slightly higher at the higher current density end of the panel. This fact is borne out in plating practice also by the build up of nodules along the edge of the panel and in the position of maximum nodule concentration on the flat panel.

At this point it seemed that the most logical electrolytic phenomenon to consider was the very broad field of polarization. Polarization which may be defined as the change in potential experienced by an electrode immersed in an electrolyte under the impetus of an applied current, is a phenomenon attendant upon all electroplating operations and has been the subject of widespread exploratory research. Even today research continues in an effort to verify and explain certain phenomenon associated with polarization. It has been fairly well established at the present time that polarization: 1. Increases with current density. 2. Increases with the duration of electrolysis for a constant current density. 3. Decreases with an increase in temperature. 4. Decreases with agitation. 5. Depends upon the nature of the electrode surface. 6. Varies with the material of the electrode.

No single existing theory of polarization is in agreement with all six of these generalizations; however, the theory of concentration

polarization is in harmony with the first four of these statements (28). This form of polarization which has been well established results in a thin layer of solution adjacent to the electrode, the concentration of which differs from that of the bulk of the electrolyte. This layer may be called the diffusion layer and its apparent thickness depends on those factors which influence the rate of diffusion. In an effort to determine the effect of copper ions on this polarization or overvoltage factor, measurements were taken of voltage versus current with increasing amounts of copper in solution. These values were obtained using existing laboratory equipment which unfortunately proved to be inadequate for the requirements and the test was abandoned.

When a solution contains two or more kinds of positive ions such as we have here following the copper impurity additions, then on electrolysis the deposit may contain one or both of the metals (or hydrogen) depending on the circumstances. Since all aqueous solutions contain the positive ion hydrogen in addition to any metallic ions which may be present, a consideration of the behavior of hydrogen is in order. When a hydrogen ion is discharged at the cathode the resulting atom: 1. May remain as such. 2. May unite with another to form a molecule. or 3. May unite with the electrode material to form a "hydride", solid or gaseous, which may be either a definite compound or an absorption complex. The compensating removal of the gas may occur by: 1. Diffusion of the gas into the electrode. 2. Diffusion into the electrolyte. 3. Chemical action (if oxygen or an oxidizing agent is present). or 4. Bubble formation. This latter process by which hydrogen escapes as a gas is the most important

means of hydrogen release and is a major factor in overvoltage. It is well known that this process does occur and that the solution pH rises in the vicinity of a cathode operating at less than 100% current efficiency. This rise in pH has been demonstrated by several investigators (29) (30) (31). The consequences of this increase of pH in the vicinity of the cathode are of extreme importance since some metals, including nickel, form insoluble hydroxides and basic salts at pH values of about 7. Most bright nickel plating solutions, including the one used in this investigation, are operated at a much lower pH than this, namely in the 3-4. Therefore even though considering the pH rise within the cathode film the possibility of such hydroxide or salt formation of the cathode surface is rather remote in as much as the differences encountered here would be very unlikely to boost the pH to the value of 7. However, if by some solution adjustment these hydroxides were able to form at a lower pH, their presence could be a very real consideration. In the event of their formation these particles of hydroxide or basic salt would probably be extremely small in size (of colloidal dimensions), and if these sub-microscopic particles carried positive charges, they would be transported cataphoretically to the cathode where their charges would be neutralized. Simultaneous with this discharge of colloidal particles, metal would continue to be deposited by the usual process and could conceivably form around these hydroxides and entrap them.

This sort of nickel solution alteration by which nickel hydrates* are permitted to form at lower pH levels has received some attention in Russia. In experiments there it has been demonstrated that a

*Hydroxides or basic salts.

number of factors tend to effect a change in the pH level of beginning hydroxide formation (32). It was shown that such things as the concentration of nickel sulfate, NaCl additions, boric acid concentrations, and temperature all have a definite effect on the pH at which nickel hydrates begin to form. The pH at the instant a hydrate begins to form was investigated by plotting potentiometric titration curves. The circuit in which the measurements were made included a glass electrode and two saturated calomel electrodes which were connected to the test solution or to the solution filling the glass electrode by means of an electrolytic switch. All measurements were made at a temperature of 50 ± 2°C with a RAPS type potentiometer, using a sensitive mirror galvanometer. The instant at which the hydrate began to form was likewise checked by the scattering of light in a Tyndall Cone. The light scattering was manifested at the same point as the sharp bend on the titration curves, though in ordinary light the solutions appeared to be still completely transparent, turning cloudy only after appreciable amounts of alkali were added.

The solution used in this investigation was that which is employed for the electrolytic refining of nickel and which consists of nickel sulfate, sodium sulfate, boric acid, and sodium chloride. This solution does not duplicate our electroplating solutions but the similarity is close enough so that direct comparisons may be made. Summarizing the particular results of this investigation which pertain to the problem at hand we find that the pH at which nickel hydrate begins to form is lowered somewhat by increasing the nickel ion concentration. Boric acid shows a marked effect in lowering this pH value, while sodium chloride additions and temperature increases both have a slight effect in this same direction. Translating these results into values which would pertain to the bright nickel bath used here, the possibility of hydroxides forming at the cathode layer now becomes more of a consideration since the pH differences are reduced. According to these data it may be estimated that it is possible for the pH of beginning nickel hydrate formation in bright nickel plating solutions to approach a value as low as 5.5.

The above results are very revealing and offer a great deal of information which may be useful in formulating a possible explanation for certain poor deposits; however, the detrimental effects we are concerned with are due to the addition of copper ions to the nickel plating bath. What then is the effect of these copper ions on the electrolyte since all indications so far point to a solution adjustment of some type? In a second article from this same Russian laboratory, the effect of several metallic impurities in a nickel solution upon the pH of beginning hydroxide formation was studied.(33). The experimental techniques employed were the same as described above and included in the list of impurities studied was the copper ion. To explain the behavior of copper in the nickel electrolyte different amounts of copper, in the form of $CuSO_4 \cdot 5H_2O$, were introduced into a nickel electrolyte of the composition $NiSO_4 \cdot 6\ H_2O$ - 40.6g/liter, Na_2SO_4 - 40g/liter, NaCl - 5g/liter, and H_3BO_3 of two concentrations 0 and 20g/liter. The first break in the curve obtained by potentiometric titration with a glass electrode and the appearance of a diffused glow in the Tyndall Cone were regarded as the beginning of copper hydroxide formation since it has been demonstrated that copper hydroxide will precipitate before the formation of nickel hydrates (34). The pH values at the beginning of copper hydrate formation in relation to the concentration of the copper were determined. It was found that with a copper content of 0.004g/liter the titration curve had the same appearance as the titration curve of nickel sulfate, and the pH value at the beginning of hydrate formation agreed with that for nickel. However, when the copper content of the solution was increased to 0.05 and 0.19g/liter, the pH value at the beginning of hydrate formation was noticeably lowered. The presence of boric acid likewise tended to lower this pH level as was the case with nickel.

Considering now the significance of these investigations in relation to the results already obtained from the chemical analysis of the nodules and the smooth deposit, the current density study, the various plating studies involving buffing and plating, multilayer deposits, and solution agitation changes, and finally the nodule cross-section studies, it is possible to formulate certain conclusions regarding nodule formation. First of all the plating experiments and the dependence of nodule position on solution direction furnished strong evidence that nodule formation is not a problem originating with the base metal. The structure of the nodules revealed a central core of a dark etching material surrounded by what gave every indication of being electrodeposited nickel. Even the striated bright nickel structure was in evidence in this outer nodule material. Chemical analysis of the nodules and smooth foil revealed more copper in the

nodules than in the smooth bright deposit. This would indicate that the dark core material contained more copper than the surrounding structure.

Having eliminated the possibility of a base metal dependence it became apparent that consideration should be given to the changes occurring in the plating solution following the addition of copper as an impurity. The pH of the solution was maintained at 3.75, consequently it was difficult to postulate the formation of copper or nickel hydrates. However, a consideration of polarization effects at the cathode surface indicated the possibility of a significant alteration of pH within a very thin envelope surrounding the cathode. This increase in pH coupled with the information that boric acid and an increased copper concentration both tend to lower the pH at which copper or nickel hydrates will form, points very strongly toward the presence of copper or nickel hydrates within this cathode film. If these hydrates are forming in the cathode film then the preferred location of the nodules which depends upon the solution agitation direction could be the result of a simple mechanical pressure on the film layer which would tend to move these hydroxides or hydrates closer to the cathode surface. In the rectangular tank used in these studies the solution travels from the anode to the cathode along one side and then moving across the surface to the other side and continuing on back to the anode. If hydroxides or basic salts are forming adjacent to the cathode they probably are produced in a colloidal condition and carry a positive charge. Therefore it is reasonable to assume that they would be electrodeposited on the cathode together

with the normal metal. This build up of hydrate surrounded by nickel metal proceeds at a rate far exceeding the normal deposition of metal alone. Assuming that these hydrates do form there are several possible reasons for this rapid growth behavior. First of all it seems logical that the polarization at these particular sites of compound deposit has been lowered resulting in localized areas which are more receptive to further deposition. Very possibly this more receptive nature is limited to further basic salt deposition so that the build up of a spur results. As the normal depositing metal encounters such an area it is forced upwards and the ultimate result is the cored type nodule which we observe.

A second possible explanation for this apparent uncontrolled growth centers around the fact that from the surface of a particle of deposited hydroxide hydrogen may possibly be liberated as a gas more easily than from the pure metal. This localized increase in hydrogen evolution would in turn result in an increased concentration of hydroxyl ions which means a more basic pH value and thus further hydrate or basic salt formation.

Thirdly, and equally as significant a possibility relates to the current density increase which is associated with sharp edges or projections. Thus nodules once they have started will experience a greater current density and consequently more rapid cathodic reactions. The Hull Cell tests and actual plating operations have indicated that nodule formation is somewhat favored at the higher current density areas.

A comparison of these nodules with the roughness produced when

calcium is present in the nickel solution in excess of the saturation limit, reveals that the two are entirely unrelated. The typical treed structure observed when copper is the impurity is not found in the calcium produced roughness. Further the roughness produced by calcium occurs mainly on the horizontal lip of the panels indicating more of a settling mechanism than any polarization phenomenon. Beside other differences such as size, shape, and location of the nodules or projections it is usually the case that the calcium produced roughness can be alleviated by a filtration and pH adjustment treatment; such is not the case with copper in solution. The logical explanation for calcium produced roughness is the occlusion and entrapment of precipitated salts, probably calcium sulfate.

CONCLUSIONS

The problem of determining the mechanism involved in nodule formation when copper is present in a nickel plating solution was pursued by investigating all the possible factors which relate to this anomaly. Crystallography and atomic considerations of copper and nickel eliminated the possibility of a lattice disturbance phenomenon. Photomicrographs of the cross section of these growths revealed a central core extending throughout the nodule surrounded by an apparent nickel sheath. The possibility that these nodules originated at imperfections in the base metal was disproven by several experiments. The first consisted of depositing a nickel film from a purified nickel solution and then adding copper to the solution as the deposition continued. Other experiments consisted of buffing one half the panel prior to deposition; taper sectioning the rough, black deposit; and finally altering the direction of solution agitation. In each case the results repudiated a base metal dependence for the nodules.

Polarization studies and the likely formation of hydrates resulted in a logical explanation for nodule growth. This expanation was reinforced by a chemical analysis of the nodules as well as the smooth nickel foil which revealed a slightly higher copper content in the nodules. Additional support was obtained by current density considerations which involved the use of the Hull Cell and indicated that nodule formation was increased at higher current densities.

Thus by the elimination of all other possible factors which could produce these nodules all the evidence points to the fact that the roughness in electrodeposited nickel caused by copper as an impurity results from a complex solution adjustment at the cathode surface resulting in a pH precipitation and localized polarization differences with subsequent deposition.

A comparison of the roughness in electrodeposited nickel due to calcium as an impurity and that due to copper reveals that the two are not the same. The calcium roughness results from the occlusion and entrapment of precipitated salts, probably calcium sulfate.

The results of the investigation concerning the effects of calcium in four different nickel plating solutions on the physical properties of electrodeposited nickel may be summarized as follows:

Appearance - Both the Watts' pH 2.2 and 5.2 panels were judged to have an Eastman Gray Scale reading of 1-2, and there was no change in scale reading with increasing calcium content. There was no change in the mirror bright rating given to the organic and nickel-cobalt bright panels with increasing calcium. On panels from all four solutions there was a slight increase in roughness at the higher calcium levels.

Adhesion - The adhesion of the nickel deposits from all four plating solutions was unaffected by increasing calcium concentration.

Ductility - The Watts' 2.2 deposits showed no appreciable change in ductility over the entire range of calcium impurity. The Watts' 5.2 deposits revealed a gradual decrease in ductility with increasing calcium content. The foils from both the organic and nickel-cobalt solutions exhibited a much lower degree of ductility than the foils from either of the Watts' solutions, however, the addition of calcium to the bath had little effect on the ductility.

Hardness - As expected the bright deposits revealed a much higher hardness than the Watts' dull nickel, however, the slight variations in hardness with increasing calcium content were not considered significant.

Throwing Power - The results indicate an overall reduction in throwing power with increasing calcium content. The variations, however, are not considered significant and no clear cut trend is established.

Corrosion Resistance - Evaluation of corrosion resistance was accomplished by three different methods thereby verifying the result that calcium does not affect the corrosion resistance of any of the four types of deposit.

Removal of Calcium - Electrolyte removal, high pH precipitation, increased temperature, and precipitation with hydrofluoric acid all proved to be ineffectual methods for the removal of calcium from the four nickel plating solutions.

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