PART I

THE REDUCTION OF HEXAVALENT CHROMIUM AT A NICKEL ANODE - NICKEL SULFATE SOLUTION INTERFACE DURING ELECTROLYSIS

PART II

THE EFFECTS OF CHROMIUM IN NICKEL SULFATE SOLUTIONS ON THE PHYSICAL PROPERTIES OF ELECTRODEPOSITED NICKEL

by

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A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

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AN ABSTRACT

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John K. Werner

Part I

An investigation of the reduction of hexavalent chromium at a nickel anode-nickel sulfate solution interface during electrolysis was made to determine the site of the reduction and some of the factors influencing this reaction. The reduction of chromium (VI) by nickel metal was studied with and without electrolysis. Without an externally applied electro-motive force, the nickel metal was immersed in a buffered nickel sulfate solution containing a known amount of chromium (VI). For the experiments in which an external electromotive force was used, the anolyte containing varying amounts of chromium (VI) was separated from the catholyte by a porous porcelain membrane.

The results of these studies indicated that the reduction of chromium (VI) was due to the presence of the nickel metal whether or not it was anodically polarized and that the rate of the reduction reaction was a function of surface area and pH. Within limits, the current density had little effect when electrolytic nickel was used as the anode. When the anodic current density was increased sufficiently, the reduction rate increased sharply due to the formation at the surface of the anode of an intermediate partially-oxidized product which was readily susceptible to further oxidation by any chromium (VI) present.

Part II

Using highly purified buffered nickel sulfate solutions of four different types, the effect of the presence of chromium (III) and chromium (VI) in solution on the physical properties of electrodeposited nickel was studied. The physical properties used for a basis of comparison were: appearance, adhesion, ductility, salt-spray (fog) corrosion resistance, and throwing power and efficiency.

This investigation showed that the permissable concentration limits for chromium (VI) were lower than chromium (III) though both had similar effects. When both forms were present the adverse effects were greater than for either alone.

No effect on adhesion was noted within the concentration limits chosen and the effect on appearance and throwing power and efficiency was slight. In the case of resistance corrosion by salt spray (fog), the presence of chromium (VI) in low concentration seemed to have the opposite effect of the presence of small amounts of chromium (III). The greatest influence of the chromium in both valence states was observed in the property of ductility in which a decided decrease proportional to chromium concentration was observed.

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PART I

INTRODUCTION

In an investigation of the effect of the presence of chromium (VI) in buffered nickel sulfate solutions on the physical properties of electrodeposited nickel, it was noted that metallic nickel would reduce the chromium (VI) to chromium (III) without electrolysis. Since Nyquist (1) had reported that iron (III) ions were reduced to the iron (II) state both at the anode and cathode during electrolysis, a study of the behavior of chromium (VI) at a nickel anode during the electrolysis of buffered nickel sulfate solutions was made to determine whether or not the reduction of chromium (VI) occurred, the site of the reduction and some of the factors influencing the reaction. The effect of pH variation on the reduction of chromium (VI) by nickel in the absence of current was studied to see what changes resulted from the anodic polarization of the reducing agent.

There has been relatively little reported concerning the phenomenon of reduction occurring at an electrode which is anodically polarized at an appreciable current density. Bancroft (2) suggested that reduction could occur at a copper or zinc anode during the electrolytic reduction of $KClO_3$ in order to explain the high efficiencies obtained (about 180%). Burrows (3), by using a diaphragm to separate the anolyte from the catholyte purported to show that electrolytic reduction did take place at the anode and that the reduction was a function of the anode current density. He reported greater reduction with higher current densities (smaller anode areas carrying same total current). Brochet (4, 5, 6) objected to the term "electrolytic reduction" as used by Burrows and stated that the reduction was a chemical process consisting of a series of reactions which went on independently of the electrolysis, and did not necessarily occur at the anode surface. Tommasi (7) observed that $KClO_3$ was reduced by the metal of the anode during electrolysis using metals such as copper, zinc or lead. If an anode such as platinum was used, further oxidation would occur and all evidence of anodic reduction would disappear. Turrentine (8) cited several examples of apparent anodic reduction and cathodic oxidation but explained these "reversed electrolyses" reactions as due to secondary reactions since the primary reactions are one of oxidation at the anode and reduction at the cathode. Stevenson (9) explained the phenomenon of reversed electrolysis as a secondary reaction of substances formed by the normal oxidative reactions at the anode or reduction at the cathode. Hickling (10) supported the view that it was secondary reaction of products formed in the primary reaction of oxidation at the anode which gave rise to the "apparent" reducing action of an anode. He reported the apparent reduction of chromium (VI) and manganese (VII) at a platinum anode, explaining the reaction by the formation of H_2O_2 which has reducing properties in the acid solutions in which the reduction was observed. Bancroft (11) however, asserted that there was no basis for the assumption of the intermediate formation of H_2O_2 to explain anodic reactions.

Wesley (12) reported that in galvanic corrosion, the anode weight loss is equal to the sum of the loss due to normal corrosion and that calculated from the galvanic current by Faraday's law. Muller (13) investigated the chemical reduction of the chromium (VI) added in the form of CrO_3 by metals such as copper or zinc. He reported that in the absence of foreign anions the reduction, rapid at first, soon became very slow or ceased altogether. The cessation of the reduction was attributed to the formation of a passivating film of $Cr(OH)CrO_4$ which permitted the passage of small ions such as hydrogen but not large ions such as $CrO_4^{=}$, thereby preventing further reduction. The presence of foreign anions such as $SO_4^{=}$ or Cl^- influenced the reaction by affecting the film formation in the case of zinc but not in the case of copper. Under certain conditions, the film can be broken and the reduction, as measured by loss in weight of the metal, carried further. Kolytyrkin and Frumkin (14) found that the rate of solution of nickel in acids could be calculated by using the equation $i = F_3 - F_1$, where a positive value for i indicated a cathodic current, F_3 was the rate of discharge of hydrogen atoms, and F_1 the rate of ionization of nickel ions. They found that hydrogen ions were discharged when the nickel was anodically polarized and nickel ions dissolved when the nickel was cathodically polarized, though both reactions occurred at reduced rates.

Stareck (15) reported that chromium (VI) added in the form of chromic acid was reduced at the surface of a zinc anode during electrolysis, forming the black compound, basic chromic chromate. The reduction occurred only if the metal was activated by the passage of current, and happened simultaneously with the electrolytic oxidation of the zinc. Petrocelli (16, 17) discussed the action of an active metal, aluminum, in an acid solution containing oxidation-reduction systems during electrolysis. The effect of the oxidation-reduction system is the displacement of potentials in an anodic direction when the metal is anodically polarized. No evidence for oxidation could be found when the aluminum was anodically polarized, nor was there any evidence presented for reduction at the anode. Petrocelli (18) also developed mathematically, equations for the expression of current flow as the result of anodic and cathodic currents occurring simultaneously at each electrode, this development having been based on the mixed potential theory. Hickling (19) studied the anodic decomposition of H_2O_2 in alkaline, neutral and acid solutions. His conclusion was that the reaction was electronic in alkaline solution. In acid and neutral solutions, he postulated the reaction was one between discharged OH^- radicals and the H_2O_2.

The explanation of the phenomenon of reduction occurring at anodically polarized electrodes is still not complete. It is the purpose of this investigation to study this phase of electrode reactions in the hope that a clearer understanding will result.

EXPERIMENTAL

For the study of the chemical reduction of chromium (VI), pieces of cast nickel anodes of a given area (about 30 cm^2) were immersed in 250 ml. samples of buffered nickel plating solution containing known amounts of chromic acid. The composition of the nickel sulfate solution was: $NiSO_4 \cdot 7H_2O$ (tech.), 240 g./l.; $NiCl_2 \cdot 6H_2O$ (c.p.), 45 g./l.; Boric Acid (c.p.), 30 g./l. The pH was controlled with concentrated H_2SO_4 (c.p.) and $NiCO_3$ (c.p.). Doubly distilled water was used throughout the experiment. The pH values of the solutions ranged from 1.5 to 5.1. The solution was purified following the procedure reported by Ewing, Rominski and King (20), in which high pH precipitation, low current density electrolysis, and treatment with activated carbon were used to remove undesirable inorganic and organic impurities until only spectroscopic traces of metal impurities remained. A moderate rate of agitation produced by mechanically driven glass stirrers was maintained as uniformly as possible in all the experimental runs. All experiments were made at room temperature. Weight loss measurements were made using cast nickel immersed in nickel sulfate solutions with and without hexavalent chromium to determine the effect of the chromium (VI) on the corrosion of the nickel and the correlation between the weight of nickel lost and the amount of chromium (VI) reduced.

Chromium (VI) concentrations, and occasionally the total chromium concentrations, were determined at regular intervals by the procedure developed by Serfass and Levine (21). The method for chromium (VI) was a colorimetric procedure in which the color developed by the complex of chromium (VI) with diphenyl carbazide dissolved in absolute alcohol was measured using a Klett-Summerson colorimeter equipped with a green filter. A linear relationship between the color developed and the chromium (VI) concentration was found from 0-50 μg CrO_3 per sample. The error was found to be five per cent or less. The determination of the total chromium concentration required the oxidation of the lower valence state(s) present to the hexavalent state. The procedure of Serfass and Levine was slightly modified in two respects: (1) since no iron could be detected, the steps for its removal were omitted, and (2) the use of perchloric acid to oxidize objectionable organic material was avoided by the use of a nitric-sulfuric acid mixture which was evaporated to fumes. The procedure resulted in an unavoidable error due to the incomplete oxidation of all the chromium present. This error was found to be proportional to the amount of chromium present; but by carefully standardizing the procedure, good precision with a relative error of approximately five per cent was obtained.

For the investigation of the reduction of chromium (VI) at an anodically polarized electrode, the apparatus for the electrolysis consisted of a 1000 ml. beaker which contained a 400 ml. porous porcelain cup to act as a diaphragm. The anodes consisted of rods cut from cast nickel plating anodes containing a small amount of carbon as an aid to uniform corrosion and rods and foils of nickel electrodeposited from the highly purified buffered nickel sulfate solution. These anodes were centered in the porous cup containing 350 ml. of purified nickel sulfate solution as anolyte. The catholyte consisted of approximately 350 ml. of the same solution. The cathode consisted of a sheet steel strip approximately five cm. in height surrounding the porous cup at an average distance of 1.5 - 2 cm. to avoid the possibility of shielded areas on the anode.

All electrolyses were made at room temperature. The anolyte was agitated by mechanically driven glass stirrers and the rate of agitation was kept as uniform as possible. In runs in which efficiency calculations were made, a copper coulometer was connected in series with experimental bath. The experimental conditions that were varied were: current density, pH, chromium (VI) concentration, and anode material and area.

RESULTS

The effect of pH on the chemical reduction of chromium (VI) by metallic nickel is illustrated in Figure 1. At a pH of 2 and below, under existing experimental conditions, the rate of the reduction of chromium (VI) was relatively rapid and the reduction of the chromium continued until the presence of hexavalent chromium could no longer be detected. As the initial pH was raised from 2.0 to 3.2, the reaction rate became slower. The duration of the reduction reaction became shorter. At a pH of 2.2, the reaction rate became slow in about seven to ten hours; at a pH of 2.58, the reaction apparently ceased in a little over two hours; and at a pH of 3.2, the reaction was completed, as far as could be detected, in 0.25 - 0.75 hours. Above a pH of 3.5 little or no reduction of chromium (VI) would occur at all. The pH rose in all cases where reduction occurred; if it rose sufficiently, the reaction was retarded and finally stopped. This inhibition of the reaction could be overcome in three ways: (1) by adding sulfuric acid to the experimental solution to decrease the pH; or (2) by removing the nickel metal and making it anodic in an electrolytic cell for a short period of time; or (3) by immersing the nickel being used as the reducing agent in concentrated acid, rinsing and replacing. In this last instance, a mineral acid (concentrated or dilute HCl) was found to be more effective than an oxidizing acid (concentrated or dilute nitric acid). At no time during this phase of the investigation was any visible precipitate formed in the solution or film on the anode. If a film formation was the mechanism

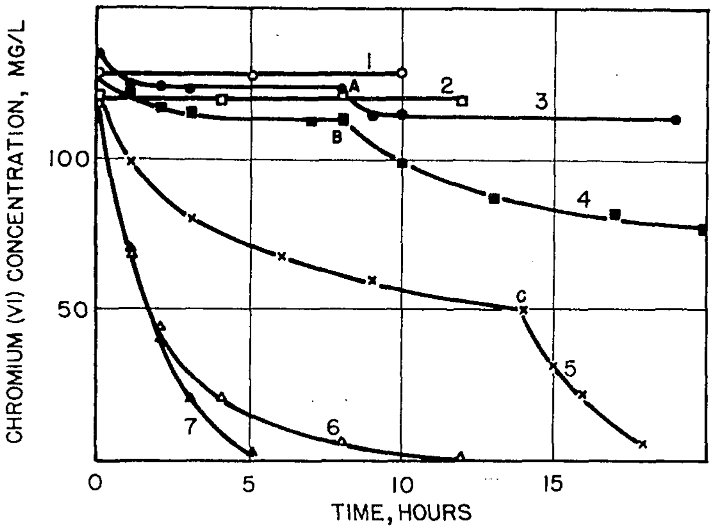

FIG. 1 EFFECT OF pH ON THE REDUCTION OF CHROMIUM (VI) BY METALLIC NICKEL (30 CM^2 AREA) IN THE ABSENCE OF CURRENT DUE TO ANY EXTERNAL EMF

1. INITIAL pH, 5.10; 2. INITIAL pH, 4.48;
3. INITIAL pH, 3.20; AT A ANODE ELECTROLYTICALLY ACTIVATED; FINAL pH, 3.84;
4. INITIAL pH, 2.58; AT B pH, 2.84; DROPPED pH TO 2.40 WITH CONC. H_2SO_4;
5. INITIAL pH, 2.20; AT C pH, 3.20; DROPPED pH TO 2.20 WITH CONC. H_2SO_4;
6. INITIAL pH, 2.05; FINAL pH, 2.85;
7. INITIAL pH, 1.50; FINAL pH, 1.82

by which the reaction was retarded, the film was soluble in acid or deformed by the addition of acid, so that reduction could go on at the initial rate. The film could also be removed electrolytically by anodically polarizing the metal.

An alternative view would be that a definite concentration of hydrogen ion was necessary to activate the nickel metal and the lower concentrations, the reduction ceased due to inactivation of the metal. This did not appear to be the case since the reactions became very slow at pH values appreciably below that at which no reduction would be seen. In the case where the initial pH was 2.58, the reaction had become slow by the time the pH had risen to 2.90. Yet noticeable reduction occurred at a pH of 3.20 for a short period and after the reduction had ceased or become very slow, the pH continued to rise. The mechanism of film formation postulated by Muller (13) appeared to apply in this case.

Weight loss measurements indicated that the presence of chromium (VI) in solution speeded the dissolution of metallic nickel. When nickel was immersed in a solution at a pH of 2.0 containing chromium (VI), it was found to lose weight at a rate seven times that of nickel immersed in a solution of the same pH containing no chromium (VI). The increase in weight loss of the nickel was accompanied by a reduction of chromium (VI) which was the equivalent of the nickel dissolved.

The chemical reduction of chromium (VI) at anodically polarized cast nickel is shown in Figures 2, 3, 4, 5 and 6. Figures 2, 3, and 4 illustrate the effect of current density on the rate of reduction of

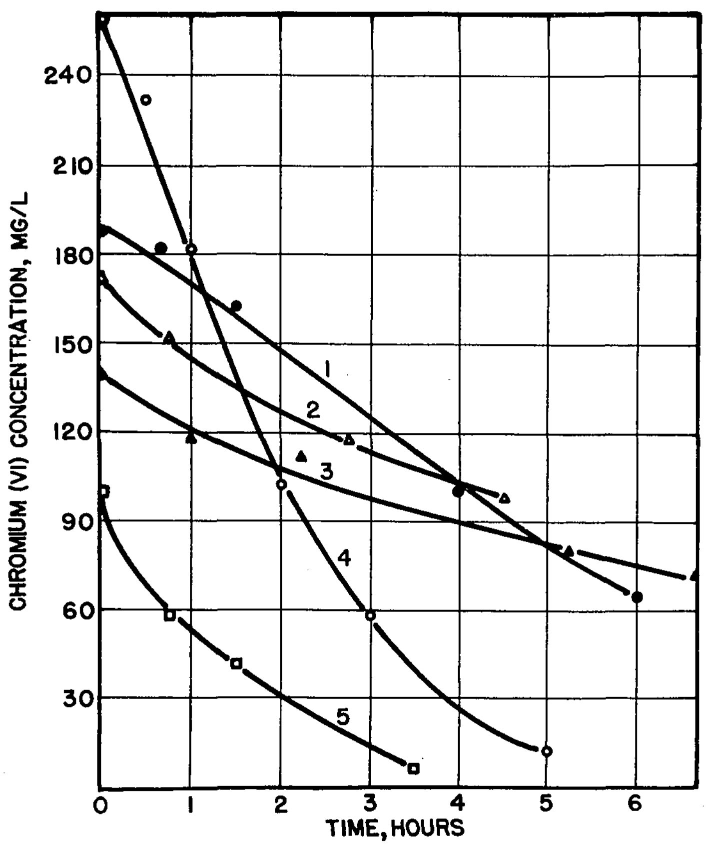

FIG. 2 EFFECT OF CURRENT DENSITY ON THE RATE OF REDUCTION OF CHROMIUM (VI) AT A CAST NICKEL ANODE

pH RANGE: 2.0-2.5; ANODE AREA: 15 CM^2

1. 85 MA/CM^2; 2. 28 MA/CM^2; 3. 39 MA/CM^2; 4. 390 MA/CM^2; 5. 220 MA/CM^2

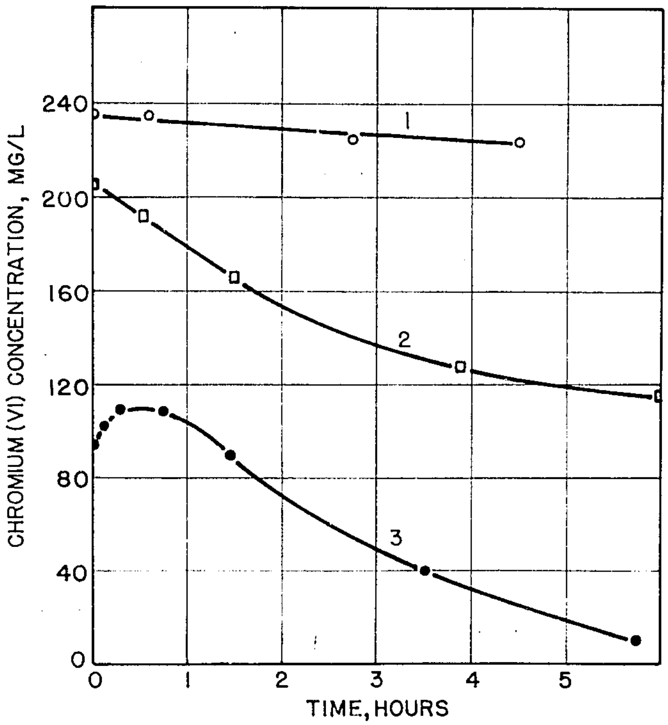

FIG.3 EFFECT OF CURRENT DENSITY ON THE REDUCTION OF CHROMIUM (VI) AT A CAST NICKEL ANODE

1. 28 MA/CM^2; PH 3.8-4.05
2. 85 MA/CM^2; PH 3.8-4.40
3. 365 MA/CM^2; PH 3.7-4.40

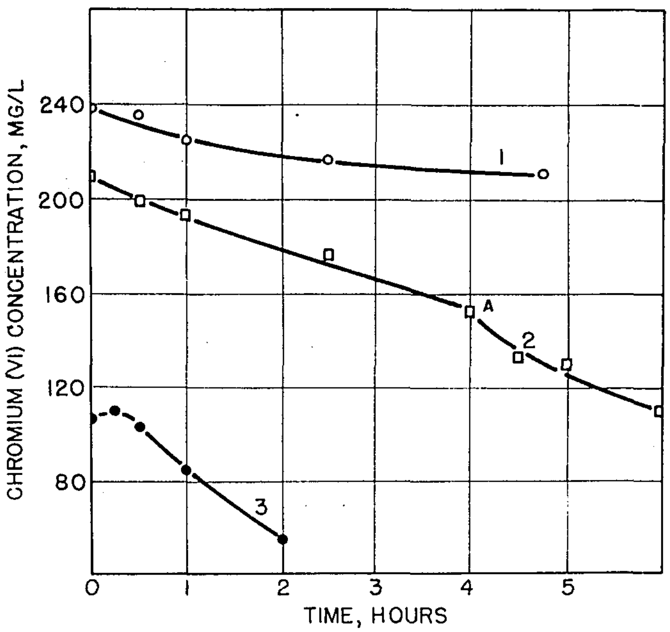

FIG.4 EFFECT OF CURRENT DENSITY ON THE REDUCTION OF CHROMIUM (VI) AT A CAST NICKEL ANODE

1. 28 MA/CM², pH 4.80-5.05
2. 85 MA/CM², pH 4.80-4.90; AT A C.D. INCREASED TO 100 MA/CM²
3. 550 MA/CM², pH 4.95-5.30

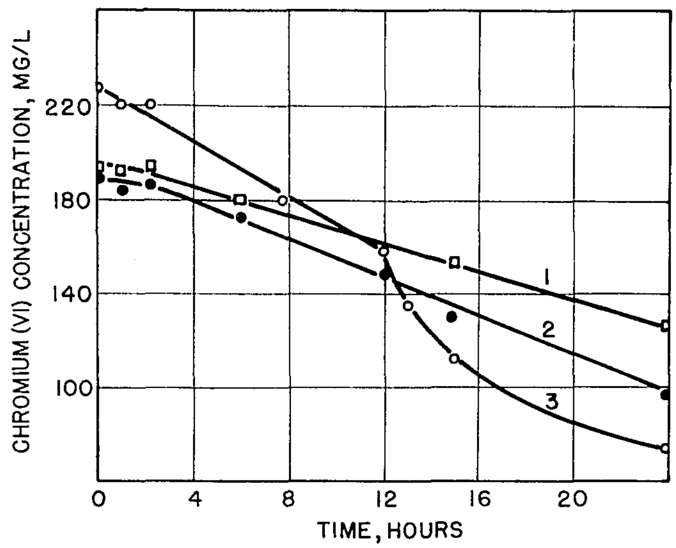

FIG. 5 EFFECT OF pH ON THE REDUCTION OF CHROMIUM (VI) AT A CAST NICKEL ANODE (CURRENT DENSITY 85 MA/CM^2)

1. pH 4.90
2. pH 3.90
3. pH 2.50

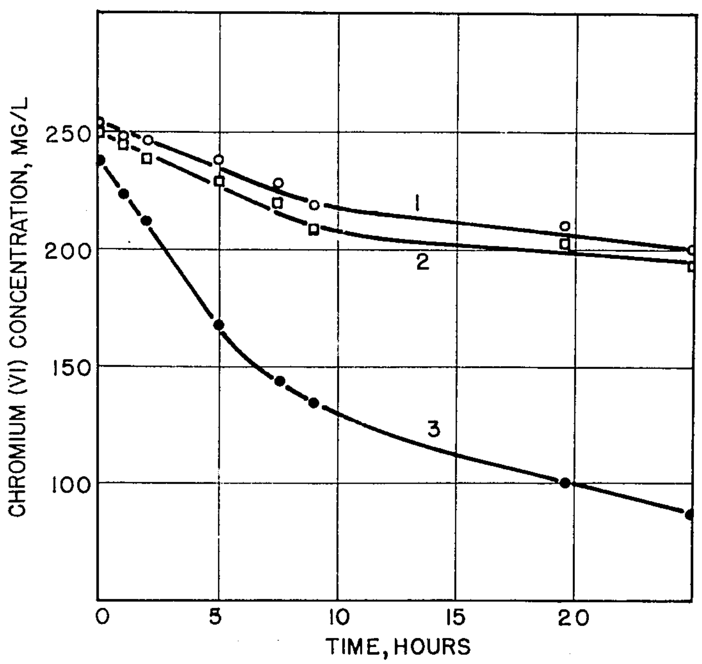

FIG. 6 EFFECT OF pH ON THE REDUCTION OF CHROMIUM (VI) AT A CAST NICKEL ANODE (CURRENT DENSITY, 28 MA/CM²)

1. pH 5.10
2. pH 4.20
3. pH 2.20

chromium (VI) in solutions having different pH ranges. In Figure 2, the effect of current density is shown when the pH of the solution was maintained close to a pH of 2.2, a value at which chemical reduction in the absence of external emf. was fairly rapid. The reduction rate was affected by current density changes, increasing as the current density was raised. At current densities up to 38 ma/cm^2 the rate of reduction compared favorably with reduction in the absence of current, though the area was approximately 15 cm^2, one half that used in the absence of current. Figures 3 and 4 show the effect of current density for pH ranges 3.70 - 4.40 and 4.75 - 5.30 respectively. It was found that in these pH ranges reduction of the chromium (VI) occurred, the rate being proportional to the current density. The passage of the current was shown to keep the nickel surface active permitting reduction to occur at pH's where no reduction could be detected in the absence of the current. Figures 5 and 6 illustrate the effect of pH on the reduction rate of the chromium (VI). The rate of reduction became slower as the pH rose but did not become zero at pH values well above that at which reduction ceased when no external current was flowing. While the change in reduction rate with increasing pH above a pH of 3.9 was slight, a pronounced effect appeared between a pH of 2.2 and 3.5. Table I presents in tabular form, the effect of changing the pH and the current density. Here again is noted the slight effect of pH change above 3.5 and the relatively large change between a pH of 2.0 and 3.5. From the data obtained, it appeared that the reduction rate approached a maximum value as the current density was raised and/or the pH lowered.

TABLE I

Effect of pH and Current Density on the Reduction of Chromium (VI) at Cast Nickel Anodes

Current Density ma/cm^2	Rate of Reduction pH 4.8 - 5.0 mg/l per hour	pH 3.8 - 4.0 mg/l per hour	pH 2.2 - 2.4 mg/l per hour
28	5	4	12.5
85	15	16	25
550	30	25	22*

* 330 ma/cm^2

As shown by curve three in both Figure 3 and Figure 4, an oxidation of chromium (III) occurred at high anodic current densities. The oxidative process appeared to be short-lived. Within a short time, the reduction of chromium (VI) became the principle reaction and the concentration of chromium (VI) decreased relatively rapidly. This oxidative effect was noticeable only under the following conditions: (1) chromium (III) was present in appreciable amounts at the start of the electrolysis; (2) the pH of the solution was above 3.2, that is, a pH at which the passage of current was necessary for continuous reduction. In the absence of chromium (III) or in solutions sufficiently acid, the oxidation could not be detected.

At high current densities the reduction of chromium (VI) is felt to be due largely to some secondary reaction and not due entirely to the metal of the anode. At a sufficiently high pH, there appeared to be a competition between reactions involving the oxidation of the chromium

(III) at the anode and the reduction of chromium (VI) by some intermediate formed by another oxidative reaction at the anode. Initially, both reactions occurred and a noticeable increase in chromium (VI) concentration was seen. When a sufficient concentration of the necessary intermediate had been reached the oxidation of the chromium (III) apparently ceased, hidden by the faster reduction of the chromium (VI) in the secondary reaction.

Whenever the operating pH of the test run was above a pH of 4.2, a precipitate appeared shortly after the electrolysis was begun. The precipitate, presumed to be some form of chromium (III) hydroxide, had no discernible effect on the reduction rate. It is believed that the action of the current was to cause the positively charged chromium (III) ions to move far enough from the metal surface so that their precipitation as $Cr(OH)_3$ or $Cr(OH)CrO_4$ could not form an impervious film which would prevent further reduction.

Reduction of chromium (VI) at electrodes of electrolytic nickel anodically polarized was found to be appreciably slower than at electrodes of cast nickel. The effect of current density was much less pronounced; very slight increases, if any, in the rate of reduction with increasing current density being shown. Figure 7 shows the effect of variation of current density and of pH. The effects of pH change were slight but in the same direction as those shown when cast nickel was used. Cast nickel appeared to have a stronger reducing action than electrolytic nickel. In Table II, a comparison of the effect of cast nickel with that of electrolytic nickel electrode is given. Here

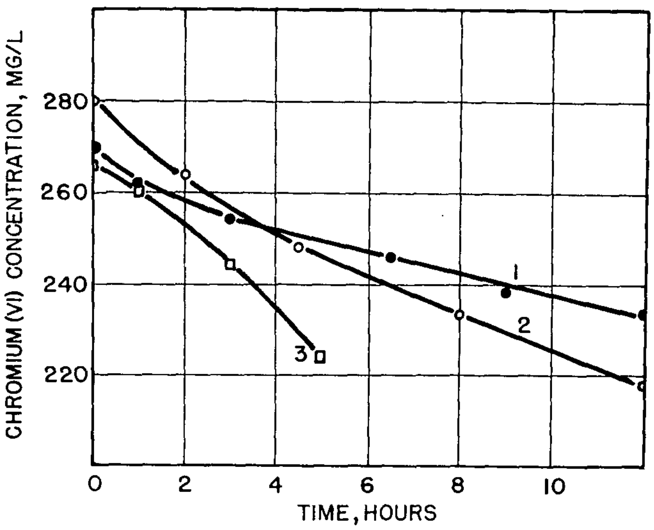

FIG. 7 REDUCTION OF CHROMIUM (VI) AT AN ELECTROLYTIC NICKEL ANODE

1. pH 5.00; CURRENT DENSITY 135 MA/CM^2
2. pH 2.00; CURRENT DENSITY 65 MA/CM^2
3. pH 2.00; CURRENT DENSITY 135 MA/CM^2

effects previously reported, i.e., increasing rate of reduction with current density, with a faster rate at cast nickel anodes than electrolytic, are seen. Figure 8 shows the more rapid reducing effect of the cast nickel and the slight effect of changing the pH when electrolytic nickel anodes were used.

TABLE II

Comparison of the Rates of Reduction of Chromium (VI) at Cast and Electrolytic Nickel Anodes During Electrolysis

	Commercial Nickel			Electrolytic Nickel	
Anode ma/cm^2	Chromium (VI) Reduced mg/l per hour	pH	Anode ma/cm^2	Chromium (VI) Reduced mg/l per hour	pH
28	11	2.0	65	6	2.0
28	12	2.0	135	8	2.0
85	25	2.0	135	3.4	5.0
330	22	2.0	660	20	2.0

In Table III, a comparison is made between reduction of chromium (VI) with and without electrolysis. The effect of the electrolysis was to enable the reduction of chromium (VI) to occur at higher pH values than without electrolysis. The rate of reduction above a certain pH varied slightly and approached a maximum as the pH was lowered. The latter effect was also shown by nickel in the absence of electrolysis.

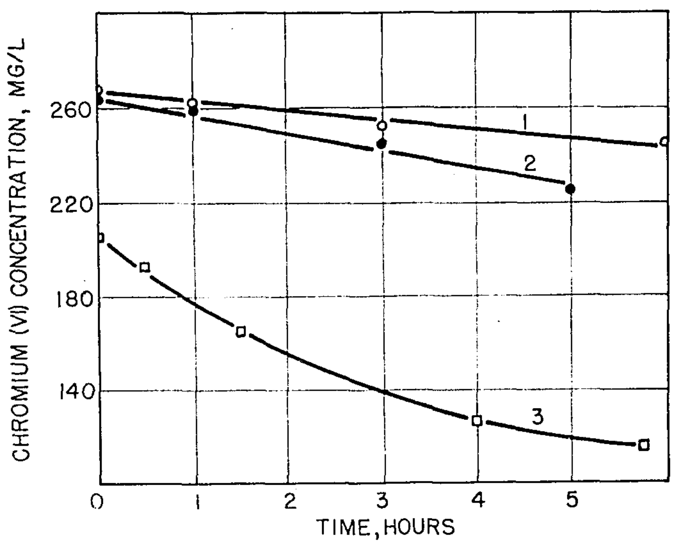

FIG. 8 REDUCTION OF CHROMIUM (VI) AT THE ANODE DURING ELECTROLYSIS

1. ELECTROLYTIC NICKEL ANODE; CURRENT DENSITY, 135 MA/CM^2; pH, 5.00
2. ELECTROLYTIC NICKEL ANODE; CURRENT DENSITY, 135 MA/CM^2; pH, 2.00
3. CAST NICKEL ANODE; CURRENT DENSITY, 85 MA/CM^2; pH, 3.80

TABLE III

Comparison of Rates of Reduction of Chromium (VI) by Nickel When No External emf. is Applied and When the Nickel is Anodically Polarized (28 ma/cm^2) At Various pH Values

pH	With Electrolysis (Anode Current Density-28 ma/cm^2) mg/l per hour	Without Electrolysis mg/l per hour
5.1	3.5	0.0
4.8	5.8	-
4.48	-	0.0
4.20	5.5	-
3.70	3.3	-
3.20	-	11 mg/l in first 0.75 hours no change after that
2.58	-	3.3
2.2	17.5*	13.8‡
2.2	32.5+	-
2.05	-	22.5
1.5	-	26.3

* Initial concentration Cr (VI) = 175 mg/l

+ Initial concentration Cr (VI) = 250 mg/l

‡ Initial concentration Cr (VI) = 120 mg/l

In this study as shown in Table IV, a fairly constant rate of reduction per unit area was found with electrolytic nickel as the anode material.

TABLE IV

Rate of Reduction of Chromium (VI) as a Function of the

Area of Electrolytic Nickel Anodes in

Solutions Maintained at pH 2.0-2.2

Anode c.d. ma/cm^2	Anode Area cm^2	mg/l Cr (VI) Reduced Per Hour	mg/cm^2 per Hour Reduced
65	19	3.66	0.19
130	16	8.00	0.50
65	13	2.81	0.22
130	13	2.50	0.19
7	105	20.0	0.19
7	105	28.0	0.27

In these experiments the dependence of the reduction rate on area was shown. The results indicated that below approximately 190 ma/cm^2, the reduction was apparently independent of the current density when electrolytic nickel was used as the anode. When the current density exceeded 165 - 220 ma/cm^2 the rate of reduction increased appreciably to a limiting value, the changes being caused by a change in the mode of reduction. The sudden increase in the rate of reduction may have been due to the production of some intermediate at the anode by an oxidative process. This in turn reduced the chromium (VI). Such a mechanism was postulated by Hickling (10) for the reduction of strong oxidizing agents that may appear to take place at inert anodes in acid solutions.

In the study of the effect of the presence of chromium (VI) on the anodic efficiencies, the results showed that the action of the chromium

(VI) did not adversely effect the electrolytic solution of the anode. The efficiency of the cast and electrolytic anodes in the absence of chromium usually lay between 99.4% and 99.9%. Occasionally, it dropped to 97% or 98%, but it never exceeded 100%. When chromium (VI), was present in the anolyte, the anode efficiencies ranged from 99.4% to 101.4%, the values of 100% or greater occurring at the lower current density ranges, e.g., 7 - 65 ma/cm^2. In a few cases when chromium (VI) was present, no reduction occurred due to some unknown reason, and some other reaction preferentially occurred, e.g., the release of chlorine. Under these conditions, the efficiency was always less than 100%, dropping as low as 98%. Weight loss measurements using an anode area of 105 cm^2 , an anodic current density of 7 ma/cm^2 and a concentration of 440 - 1440 mg./l. chromium (VI) in the anolyte showed weight losses of the anodes which were in excess of 100% of the loss due to the passage of the current. The weight loss of the anode agreed fairly well with the loss that theoretically should have occurred, calculated from the amount of current passed and the amount of chromium (VI) reduced. The actual weight losses obtained were 99.2% - 99.6% of the values that should have been obtained on the basis of 100% electrolytic efficiency plus the loss due to the chromium (VI) reduced. These experiments give support to the theory that the chromium (VI) is reduced by the nickel metal even though the metal is polarized anodically by an external electromotive force.

CONCLUSIONS

The reduction of chromium (VI) to chromium (III) takes place at the nickel anode - nickel sulfate solution interface with or without electrolysis. The reduction is brought about by a reaction between the nickel metal and the chromium (VI), i.e., nickel is oxidized forming nickel ions and releasing electrons which bring about the reduction of the chromium (VI). Anodic polarization of the nickel does not hinder this reaction even at relatively high current densities. It broadens considerably the pH range in which the reduction can take place. If sufficiently high anodic current densities are employed, the mechanism of the reduction reaction for the chromium (VI) alters. The reduction is then not simply a reaction between the chromium (VI) and the nickel anode, but is the reaction of the chromium (VI) with a product of some oxidative reaction at the electrode. At these high current densities there is evidence that the oxidation of chromium (III) to chromium (VI) may occur until sufficient oxidizable products are formed by other electrochemical reactions to make the reduction of the chromium (VI) to chromium (III) the net reaction of the chromium.

The rate of the reduction of chromium (VI) at the nickel anode interface is influenced by metal purity, electrode area, and pH. Current density influences the reaction to a limited extent, depending on factors such as purity of the nickel used for the electrodes and the pH.

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PART II

INTRODUCTION

The effects of chromium as an impurity in four types of nickel plating solutions were studied and data are presented which show the accompanying changes in certain physical properties of the electrodeposited nickel. McNaughton and Hammond (1) reported that reduced cathode efficiency and stress in the deposits resulted from the presence of chromic acid in nickel plating solutions. Chromic sulfate also caused a reduction in efficiency together with a slight brightening effect. Hothersoll and Hammond (2) reported that the effect~~s~~ of chromic acid in nickel plating solutions was more accentuated at a low pH than at a high pH. Pietrafesa (3), Puri and Seth (4) and Martin (5) obtained results in agreement with Hammond and his co-workers. For the removal of chromium, precipitation at a high pH after reduction to the trivalent state with iron (II) sulfate was recommended (1). Addition of calculated amounts of lead salts, especially the carbonate was reported by Weisberg (6) and by Diggin (7) to be a method for the removal of chromium (VI). Weisner (8) showed that the equilibrium concentration of chromium (III) at a pH of 5.4 is 2 mg./l. in buffered nickel sulfate solutions. He also showed that high pH precipitation is satisfactory only for chromium present in the chromium (III) state.

In this investigation the study of the behavior of chromium was divided into two parts, each of the common valence states (III and VI) being studied separately. The nickel solutions used were described fully in an earlier paper (9). They consisted of two of the Watts type, at pH 2.2 and pH 5.2, which gave grey deposits and two which gave bright deposits: one using organic brighteners, the other being an alloy type containing small amounts of cobalt.

Since it had been reported by Nyquist (10) that nickel metal in a low pH nickel sulfate solution would reduce trivalent iron to the divalent state, i.e., the ferrous state is the more stable form, the effect of metallic nickel on the valence state of dissolved chromium was studied. It was found that hexavalent chromium, chromium (VI), was unstable, being reduced to the trivalent chromium (III) form. Experiment also showed that at 40 a.s.f. the total concentration of chromium in solution decreased noticeably only so long as an appreciable amount, i.e., about 5 - 10 mg./l., of chromium (VI) was present. When the chromium (VI) concentration dropped to 5 - 10 mg./l. detectable removal of chromium practically ceased. During these experiments it was noted that the concentration of chromium (III), in a solution originally containing only chromium (VI) as an impurity, built up during electrolysis more rapidly than the total chromium in solution was reduced. Eventually, a state was reached in which all the chromium in solution was in the trivalent state and the concentration of the chromium did not change appreciably with further electrolysis of the solution. To substantiate the electrolytic removal of chromium, analyses were made of strip deposits from solutions containing hexavalent chromium in which a drop of 40 - 50 mg./l. total chromium concentration occurred. Chromium was found in these deposits in trace amounts, though its form was not determined. When solutions containing chromium originally in the trivalent state only were electrolysed at 40 a.s.f., little or no change could be detected in the chromium concentration and at no time could any hexavalent chromium be detected.

Electrolysis at low current densities, i.e., 10 a.s.f., of solutions containing hexavalent chromium resulted in the complete reduction of the chromium (VI) to chromium (III) with no noticeable change in total chromium content, indicating higher current densities are required for the deposition of the chromium. Electrolysis of solutions which contained originally trivalent chromium, using low current densities caused no detectable change in the chromium concentration showing that at low as well as at high current density trivalent chromium is removed very slowly if at all, by electrolysis.

In this study it was noted that a concentration of 80 mg./l. or more of chromium (VI) drastically reduced the efficiency of the deposition. With sufficient hexavalent chromium present initially, the deposition of nickel would cease after a very thin, poorly adherent and discolored layer had been deposited. As the electrolysis continued, the chromium (VI) was reduced gradually; eventually, deposition of nickel was resumed, first as a nodular deposit. The nodules were widely separated initially, then became more numerous and more closely spaced. When the chromium (VI) concentration had been sufficiently reduced, the deposit became continuous though at first with poor adhesion and a tendency to flake off. Eventually sufficient reduction of chromium (VI) produced conditions under which a uniform, adherant deposit of normal appearance was produced. At this point there still remained amounts of hexavalent chromium varying from 40 - 60 mg./l. in solution.

Since it was found that chromium was stable in the trivalent state in nickel sulfate solutions and that hexavalent chromium could not be present during electrolysis without some trivalent ions being formed, it was decided to study the effect of the presence of dissolved trivalent chromium first. Having thus determined its effects, a study of the hexavalent-trivalent combination of ions would give insight to the effect of the hexavalent ions. In the latter part of the study the trivalent chromium was kept as low as feasible without spending excessive time on its removal. Generally, the chromium (III) concentration varied from 0 - 20 mg./l., with a maximum of 35 - 40 mg./l.

EXPERIMENTAL

A. Preparation of Panels and Evaluation of Physical Properties.

The methods for the preparation and purification of solutions, the preparation of deposits and the subsequent testing of the physical properties of the deposits were those described in a previous publication (9). Two modifications in the procedure for the preparation of deposits were made. The size of the vertical section of the bent cathode was reduced from 2" x 3 1/2" to 2" x 3", a change necessitated by the dimensions of the raw material available for the preparation of the panels. The second modification was the elevation of the operating temperature of the alloy-type plating solution from 55° C. to 60° C. in order to improve the bright plating range.

Since the methods for evaluating the effects of the chromium on the deposits were largely visual and involved the human element, reference panels were prepared from a pure sample of each of the four types of solutions being investigated. These pure deposits served as the basis for the evaluation of the physical properties of the specimens made from solutions containing various known amounts of chromium. Changes in the physical properties of the deposited nickel were reported as per cent changes from the norm shown by the pure standards except in the case of appearance. In judging this property two scales were necessary. For the grey deposits from the Watts type solutions the Eastman Grey Scale was used. An arbitrary scale of brightness ranging from "Mirror Bright" to "Dull" was established for the two types of bright deposits.

The concentration ranges for both hexavalent and trivalent chromium used were established individually for each type of solution since the exact effects and limits of chromium were not known. It was found that the four baths had different maxima of concentration at which satisfactory deposits could be obtained. In the case of the nickel-cobalt alloy type solution, more trivalent chromium could have been added, but it was felt sufficient to use the maximum that could be used in any of the other types of solutions. In the case of trivalent chromium the concentrations were 0, 5, 12.5, 50, 75, 125 and 250 mg./l. with the maximum concentrations for the Watts pH 5.2 solution of 50 mg./l., the organic type solution of 125 mg./l., and the Watts pH 2.2 and nickel-cobalt type solutions of 250 mg./l.

The limit for the Watts pH 5.2 solution was low because all of the chromium did not remain in solution even at the lowest concentration, e.g., 5 mg./l. and it was felt that the effects were not of dissolved chromium so much as of precipitated chromium. The limits for the Watts pH 2.2 solution and the organic type solution were chosen at 250 mg./l. and 125 mg./l. trivalent chromium respectively because at these concentrations the baths became difficult to control with respect to the pH. The pH rose very rapidly with the concentrations in the respective solutions and in conjunction with the rise in pH detrimental effects appeared such as peeling and blackening at the solution line on the vertical section of the panel, gassing, peeling and blackening of the deposit on the underside of the horizontal section of the panel. To obtain satisfactory deposits at these concentrations of trivalent chromium, the pH had to be maintained at or slightly below the specified values 2.2 for the Watts solution and 3.2 for the organic type.

In the study of hexavalent chromium much the same effects were noted at lower concentrations. The exact concentration at which the adverse effects due to hexavalent chromium appeared was greatly influenced by the amounts of trivalent present, therefore attention was directed toward keeping the chromium (III) concentration relatively low, i.e., 40 mg./l. or less. Again in the case of the Watts pH 5.2, a precipitate of the chromium (III) formed almost immediately and because of its pronounced effect on the deposit, a low limit of hexavalent chromium was set. It was impossible to exclude the effects of the precipitated chromium (III) in this case. The concentration limits at which usable deposits could be made by keeping the pH under close control and maintaining a low chromium (III) concentration were: Watts pH 2.2, 60 - 75 mg./l.; organic type, 20 - 35 mg./l.; nickel-cobalt alloy type, 40 mg./l. or slightly more.

B. Effects on Physical Properties

Part I - Trivalent Chromium

1. Appearance - Table I summarizes the effect of the soluble trivalent chromium in nickel plating solutions on the appearance of the vertical sections of the deposits from these solutions. In general, no effect was noticeable until the concentration of the chromium reached 50 mg./l. for the deposits from the Watts solution (pH 2.2) and 75 mg./l. for the bright deposits. All deposits from the high pH (5.2) Watts solution containing chromium showed roughness attributed to the presence of

TABLE I

Effect of Trivalent Chromium on the Appearance of Nickel Deposits

Trivalent Chromium Concentration mg./l.	Bath Type			
	Watts pH 2.2	Watts pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	1 1/2*	2*	Mirror Bright	Mirror Bright
5	1 1/2	2	Mirror Bright	Mirror Bright
12.5	1 1/2	2	Mirror Bright	Mirror Bright
25	1 1/2	2	Mirror Bright	Mirror Bright
50	1 1/2	2	Mirror Bright	Mirror Bright
75	1 1/2	-	Slightly Milky	Mirror Bright
125	1 1/2	-	Slightly Milky	Mirror Bright
250	1 1/2	-	-	Mirror Bright

* Step of Eastman Grey Scale

precipitated chromium. The deposits from the Watts pH 2.2 solution were finer grained and smoother than the pure deposits when the chromium concentration varied from 50 to 250 mg./l. A concentration 75 mg./l. or more of chromium in the organic type solution caused the deposits to be milky. The only effect noticed in the deposits from the nickel-cobalt alloy type solution was the increase in stress in the deposits evidenced by a bending of the panel in plating when the chromium content varied from 75 to 250 mg./l. At no time during this study did the chromium affect the very low or medium current density areas adversely.

2. Adhesion - The adhesion of the nickel deposits to the steel base metal was measured by the bend test, described in an earlier pub-

lication (9), in which the horizontal lip of the panel was creased under pressure along the short axis and the fold examined under a forty power microscope. This test, though qualitative, was the most suitable for this work, approximating satisfactorily, methods used in industry. In this study, at all concentrations used, the chromium in the trivalent state did not discernibly affect the adhesion of any deposit to the base metal as long as proper operating conditions were maintained. At the higher concentrations, 125 - 250 mg./l., the highest current density regions would show poor adhesion if improper plating conditions were used, i.e., the pH of the solution were allowed to rise.

3. Ductility - The presence of trivalent chromium as an impurity caused a decrease in the ductility of the deposits from all four types of solutions. The concentration at which the decrease first became noticeable varied for each type of solution. In the Watts pH 2.2 bath the decrease was first noticed with 12.5 - 25 mg./l. chromium present. From 20 - 250 mg./l. the decrease in ductility remained approximately the same. A continuous decrease in ductility with increase in chromium content was shown by the deposits from the high pH Watts solution starting with 5 mg./l. chromium. The loss in ductility was greatest for this type of solution. The ductility of the deposits from the organic type solution showed no change until a concentration of 25 mg./l. chromium was present. The ductility decreased then with increasing chromium concentration up to 75 mg./l., the maximum concentration at which a strippable foil could be made. A decrease in the ductility of the deposits from the nickel-cobalt alloy type solution was noticed when the chromium

content reached 50 mg./l. but did not change with further increase in chromium content up to 250 mg./l.

The test for ductility, described in a previous paper (9), consisted of repeatedly creasing with the fingers a predesignated portion of the stripped deposit until the first indications of rupture appeared.

4. Salt Spray (Fog) Corrosion Resistance - Following the procedure set forth in A.S.T.M. Specification B117-49T and the system of rating described in a previous paper (9), the change in corrosion resistance of the deposited nickel due to the presence of chromium in solution was evaluated. The deposits subjected to salt spray were compared to A.S.T.M. panels #11 (before breakdown), #9 (at break-down), and #7 (after break-down), giving a standardized procedure for the evaluation of this physical property. The test specimen were unbuffed nickel plated steel. Three thicknesses of deposits - 0.0003, 0.001, and 0.0015 inch - were made in triplicate at each concentration of chromium used. The deposits were cleaned with magnesium oxide prior to exposure to the corrosion test. The results are reported as per cent change from the breakdown time of the standard deposits made from solutions containing no chromium. The deposits were examined at one half hour and one hour intervals.

As shown in Figures 1, 2, 3 and 4, the presence of trivalent chromium in general decreased the corrosion resistance of the deposited nickel from the four types of solutions investigated. The decrease, rapid at first, leveled out as the chromium concentration increased. Within experimental error, the decrease in salt spray (fog) corrosion resistance

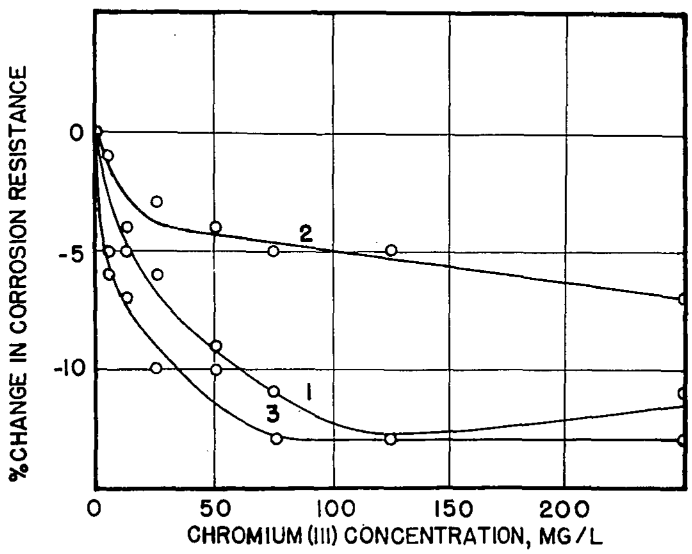

FIG.1 EFFECT OF CHROMIUM (III) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE WATTS PH 2.2 TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

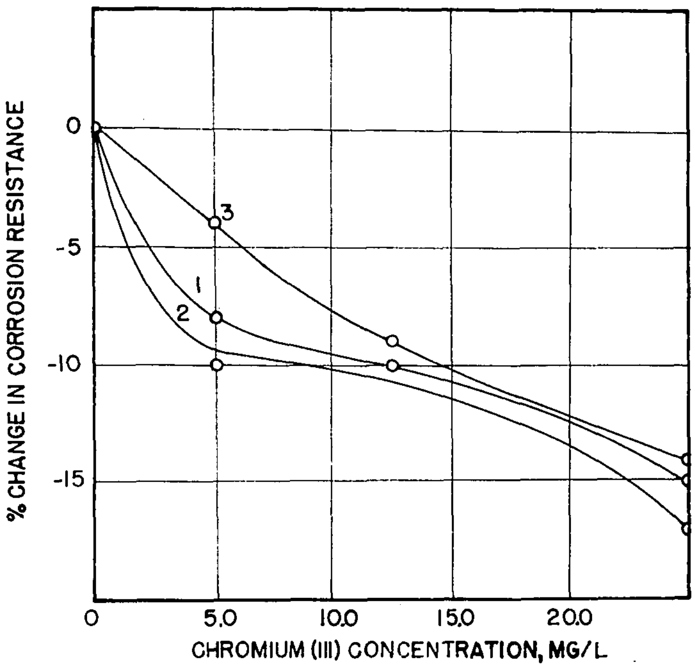

FIG. 2 EFFECT OF CHROMIUM (III) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE WATTS PH 5.2 TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

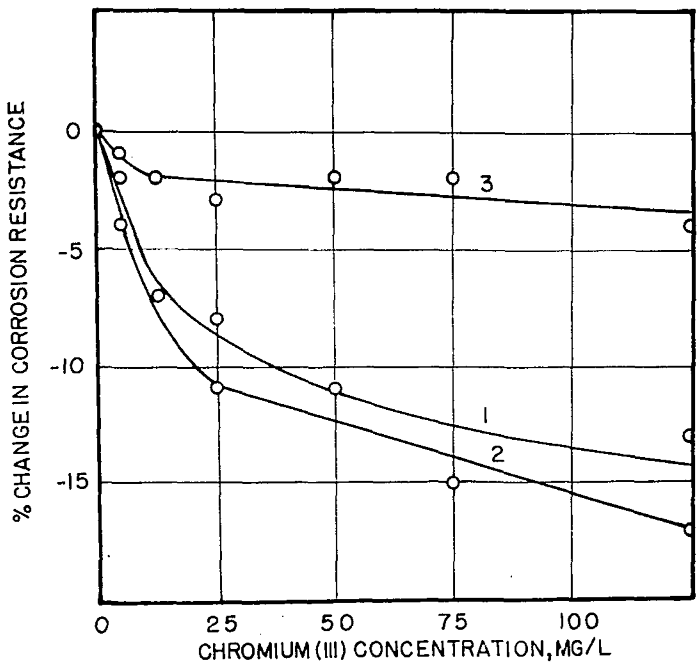

FIG. 3 EFFECT OF CHROMIUM (III) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE ORGANIC TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

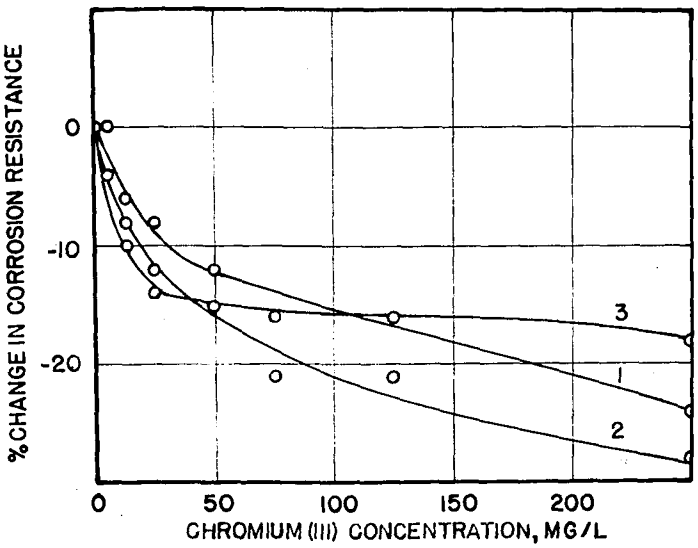

FIG. 4 EFFECT OF CHROMIUM (III) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE NICKEL-COBALT TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

was the same for the 0.001" and 0.0015" deposits. The response of the 0.0003" deposits was very similar to that of the heavier deposits except in the case of the organic type solution in which, within experimental error, little if any change was effected by the presence of chromium in solution.

5. Throwing Power and Efficiency - Since with proper pH control, no gassing was observed at the cathode during the preparation of test panels in the solutions containing chromium as an impurity, it was assumed that no change occurred in cathode efficiency and that any change in the deposit thickness was due to a change in the throwing power of the solution. Using the procedure outlined in a previous paper (1), the thickness of the deposits was measured by examining a predesignated area of the cross-section of the deposits with a Bausch and Lomb Research Metallographic microscope. Table II summarizes the results. In general, no definite trends were shown for either an increase or a decrease in this property. The throwing power tended to increase for all types of solutions investigated except the alloy type. This solution showed in general, a slight decrease over the concentration range of 5 - 250 mg./l. chromium (III). From the results obtained, it may be said that chromium in the trivalent state has no significant effect on the throwing power of the solutions used.

TABLE II

Effect of Trivalent Chromium on the Throwing Power of Nickel Plating Solutions

Trivalent Chromium Concentration mg./l.	Percent Change Bath Type			
	Watts pH 2.2	Watts pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	0	0	0	0
5	+10	+2	+10	-5
12.5	+ 3	+2	+ 2	-2
25	+12	+4	+ 3	-8
50	+ 6	+2	+ 4	-8
75	+ 8	-	+ 2	-9
125	+10	-	+ 2	-9
250	+11	-	-	-4

Part II - Hexavalent Chromium

1. Appearance - The effect of hexavalent chromium as an impurity in nickel solutions on the appearance of the vertical sections of the deposits is summarized in Table III. In general, the concentrations used, with careful control of pH and other operating conditions had little effect on the appearance of the bright deposits. At the higher concentrations, the concentration of trivalent chromium exerted considerable influence, i.e., the higher the chromium (III) concentration, the more critical were the operating conditions and the lower the permissable concentration of hexavalent chromium. In all cases, the

TABLE III

Effect of Hexavalent Chromium on the Appearance of Nickel Deposits

Hexavalent Chromium Concentration mg./l.	Bath Type			
	Watts pH 2.2	Watts pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	1-2*	1-2*	Mirror Bright	Mirror Bright
5	-	1-2	Mirror Bright	Mirror Bright
10	-	-	Mirror Bright	Mirror Bright
15	1	1	Mirror Bright	-
20	-	-	Mirror Bright	Mirror Bright
35	1	-	-	-
40	-	-	-	Mirror Bright
60	0-1	-	-	-
75	0-1	-	-	-

* Step of Eastman Grey Scale

chromium (III) concentration was kept below 40 mg./l. In the deposits from all four types of solutions increased stress was evident when the concentration of hexavalent chromium was 15 mg./l. or more, if the pH and the trivalent chromium concentration were not closely controlled.

In the deposits from the Watts pH 2.2 solution, the most pronounced effect was a whitening of the deposit as the chromium (VI) concentration increased. Roughness from precipitated chromium (III) was present in the deposits from the Watts pH 5.2 solution in addition to the whitening effect. The grain refinement and smoothing effect of trivalent chromium was not apparent in the deposits from the Watts pH 2.2 solution.

2. Adhesion - Dissolved hexavalent chromium had no discernible effect on the adhesion of the nickel deposits from the four types of solutions studied within the concentration ranges used as long as certain conditions were met. If the pH were allowed to rise too high, i.e., 0.1 - 0.2 pH above the normal operating pH of the solution, or if the trivalent chromium concentration exceeded approximately 40 mg./l., the adhesion of the deposit was adversely affected at the air-liquid interface on the vertical section of the panel and the highest current density areas of the horizontal section, i.e., the edge nearest the anode.

3. Ductility - The presence of hexavalent chromium in solution caused a decrease in ductility of the deposits from the four types of solution. In the Watts pH 2.2 solution, the decrease varied from 9% to 16% in the concentration range of 15 - 60 mg./l. chromium (VI). No ductility measurement could be made for the 75 mg./l. concentration level because a satisfactorily strippable deposit could not be obtained. In the Watts pH 5.2 solution, the decrease in ductility was great, ranging from 55% to 85% over the concentration range of 5 - 15 mg./l. The deposits from the organic type solution showed a decrease varying from 25% to 50% when 15 - 35 mg./l. of hexavalent chromium were present in solution. The decrease in ductility in the deposits from the nickel-cobalt solution varied from a value of 33% with 5 mg./l. chromium (VI) present in solution to a value of 60% with 40 mg./l. present.

4. Salt Spray (Fog) Corrosion Resistance - Because of the rapidity with which the 0.0003" deposits broke down and the large percent change

with small time intervals, the discussion of the effect of hexavalent chromium will be based mainly on the results obtained from the tests of the heavier deposits. In the case of the thin deposits, a minimum in salt spray resistance of the deposits from all of the baths was noted at the lowest concentrations of chromium (VI) used. The results from the heavier deposits did not show this. Figures 5, 6, 7 and 8 show the effect of hexavalent chromium on the salt spray (fog) corrosion resistance of deposits made from the four types of solution containing it as an impurity. In no case is there a significant effect. The grey deposits from the Watts pH 2.2 solution showed increased resistance in both the 0.001 inch and 0.0015 inch deposits. The deposits from the Watts pH 5.2 solution showed a decrease for the 0.001 inch deposits while the 0.0015 inch deposits showed a slight increase in this property. There was no change in corrosion resistance of the deposits from the organic type solution until the concentration of chromium exceeded 15 mg./l. With a concentration of 20 mg./l., the corrosion resistance decreased 10%. The effect of hexavalent chromium on deposits from the nickel-cobalt type solution was to decrease slightly the corrosion resistance when 10 - 40 mg./l. chromium (VI) were present in solution. These results indicate that the hexavalent chromium tends to counteract the effect of trivalent chromium which decreases the salt spray corrosion resistance of nickel deposits when present in small amounts.

5. Throwing Power and Efficiency - Since no gassing was noted in the concentration ranges studied (as shown in Table IV) as long as plating conditions were controlled, the efficiency was assumed to be unchanged. The test was, therefore, considered a measure of throwing power. The

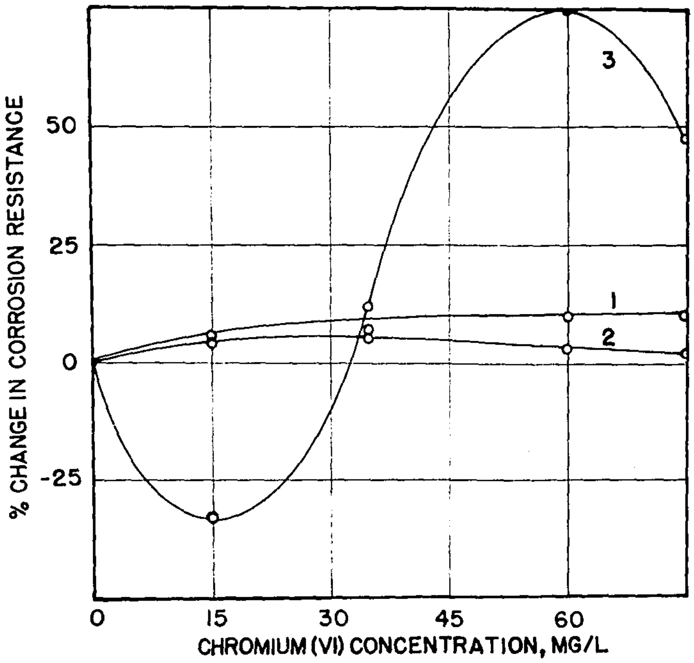

FIG. 5 EFFECT OF CHROMIUM (VI) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE WATTS PH 2.2 TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

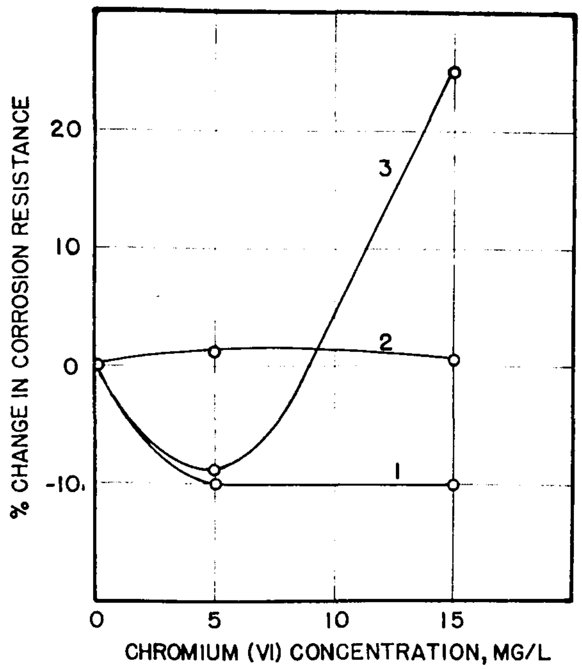

FIG. 6 EFFECT OF CHROMIUM (VI) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE WATTS PH 5.2 SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

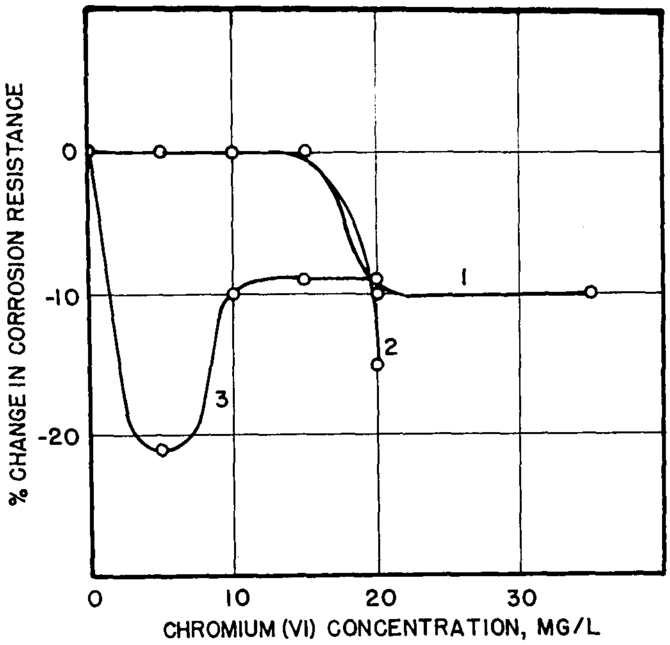

FIG. 7 EFFECT OF CHROMIUM (VI) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE ORGANIC TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

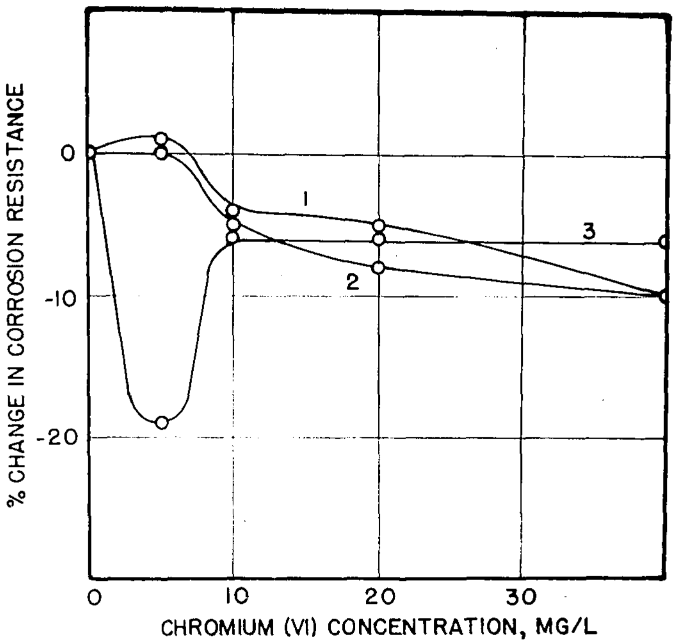

FIG. 8 EFFECT OF CHROMIUM (VI) CONCENTRATION ON THE SALT-SPRAY (FOG) CORROSION RESISTANCE OF DEPOSITS OF VARYING THICKNESSES FROM THE NICKEL-COBALT ALLOY-TYPE SOLUTION

1. 0.001 INCH DEPOSIT
2. 0.0015 INCH DEPOSIT
3. 0.0003 INCH DEPOSIT

TABLE IV

Effect of Hexavalent Chromium on the Throwing Power of

Nickel Plating Solutions

Hexavalent Chromium Concentration mg./l.	Percent Change Bath Type Watts pH 2.2	Watts pH 5.2	Organic pH 3.2	Nickel-Cobalt pH 3.75
0	0	0	0	0
5	-	+5	+3.5	-1.5
10	-	-	+2.0	-4.5
15	0	+7	0	-
20	-	-	+2.5	+0.5
35	-12	-	-	-
40	-	-	-	-1.5
60	-4	-	-	-
75	-10	-	-	-

results showed that the presence of hexavalent chromium in solution had an insignificant effect on throwing power. Table IV summarizes the effect of dissolved hexavalent chromium on the throwing power of the four types of solutions studied. The effect of the hexavalent chromium is in general to decrease the throwing power of the nickel-cobalt and Watts pH 2.2 solution and increase the throwing power of the other two. In all cases some trivalent chromium was present in varying amounts sufficient to have a slight effect. The presence of hexavalent chromium modified this effect in all but the organic type solution.

C. Removal of Chromium

1. Procedures - Two methods for the removal of the chromium were studied: electrolysis and precipitation at an elevated pH obtained by treatment of the solution with nickel carbonate. The methods of analysis for the hexavalent and trivalent chromium followed those developed by E. J. Serfass, et al (11) under the A. E. S. Research Project #2, with the following modifications in the analysis for total chromium in solution: the removal of iron was not used since the amount of iron in the original solutions was not detectable and precautions were taken to prevent contamination of the solutions with iron; perchloric acid was not used to destroy the organic material. This was done by evaporating the solution sample with a nitric-sulfuric acid mixture to dense fumes. The results obtained using these modifications were deemed satisfactory.

The procedures for the preparation and plating of the deposits and the apparatus for these purification methods were described in a previous publication (9). Standard operating conditions of pH, temperature, and rate of agitation previously established for each type of solution studied were maintained in the study of the electrolytic removal of chromium. For low current density studies, flat steel cathodes 2 x 3.5 inches were used. These were completely covered with approximately 0.002 inch of electro-deposited nickel since it had been shown in another investigation (12) that at low current densities much below 40 a.s.f., the steel cathode was not covered quickly enough to prevent the dissolution of iron and subsequent contamination of the solution. This precaution was unnecessary when current densities of 40 a.s.f.

were used since at this current density the steel cathode was covered rapidly enough to prevent dissolution of the iron in detectable amounts.

In the removal of chromium by precipitation, the procedure was to obtain pH values ranging from 2.0 - 5.5 by adding the necessary amounts of nickel carbonate to the solutions originally at a pH of 2.0. Equilibrium conditions were approached by allowing the samples to stand for at least twenty four hours before the final pH measurement was made. Experiment had shown that standing for longer periods had very slight effects on the analytical results. The samples were then filtered and analysed immediately, before further change could take place. The maximum amounts of chromium used in this procedure were 250 mg./l. for the nickel-cobalt alloy type and Watts type solutions and 125 mg./l. for the organic type solution.

2. Evaluation of Results - The electrolytic method for the removal of chromium was found to be unsatisfactory at high or low current density. It was found to reduce the hexavalent chromium to the trivalent state, but the concentration of trivalent chromium was not reduced noticeably over extended periods of electrolysis. At 40 a.s.f. a maximum change of 2 mg./l. in the trivalent chromium concentration was detected after six hours of electrolysis. When using a lower current density of 10 a.s.f., no change could be detected over more lengthy periods of electrolysis. These results indicated that electrolytic removal of chromium would involve excessive loss of nickel. Figures 9 and 10 illustrate the inadequacy of the electrolytic method.

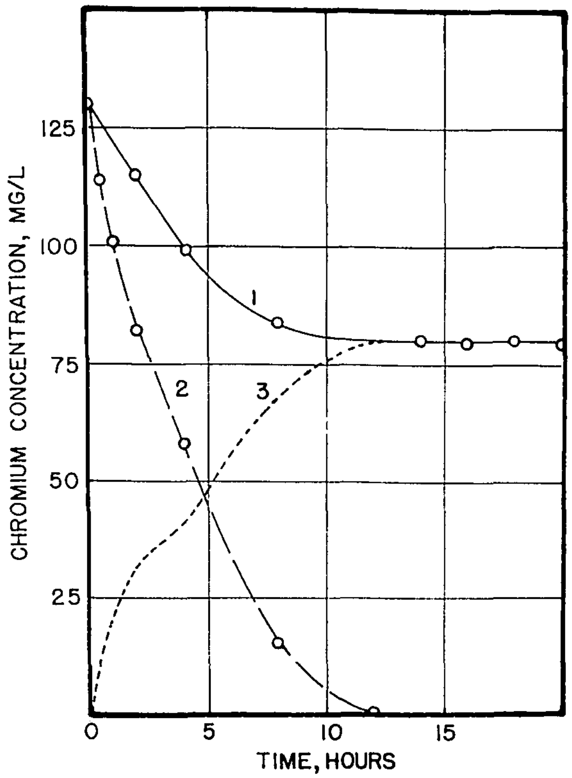

FIG.9 EFFECT OF HIGH CURRENT DENSITY (40 A.S.F) ELECTROLYSIS ON THE CONCENTRATION OF CHROMIUM ADDED INITIALLY IN THE HEXAVALENT FORM

1. TOTAL CHROMIUM CONCENTRATION
2. CHROMIUM (VI) CONCENTRATION
3. CHROMIUM (III) CONCENTRATION (BY DIFFERENCE)

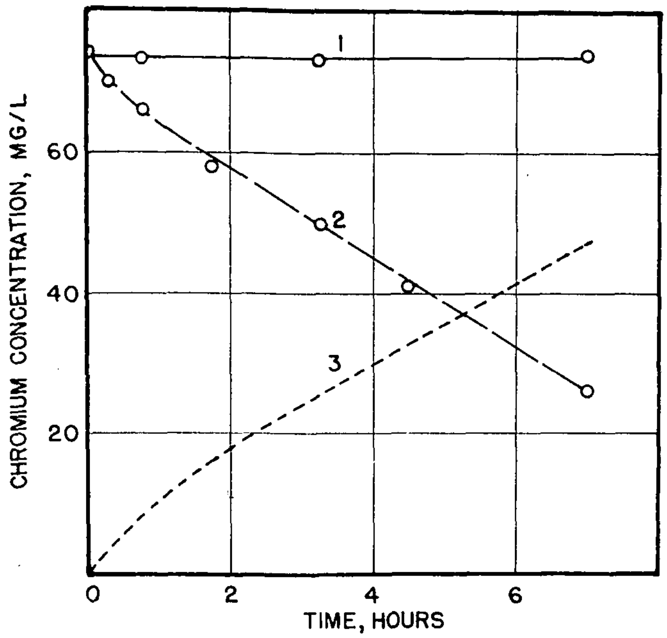

FIG.10 EFFECT OF LOW CURRENT DENSITY (10 A.S.F.) ELECTROLYSIS ON THE CONCENTRATION OF CHROMIUM ADDED INITIALLY AS CHROMIC ACID

1. TOTAL CHROMIUM CONCENTRATION
2. CHROMIUM (VI) CONCENTRATION
3. CHROMIUM (III) CONCENTRATION (BY DIFFERENCE)

The second method investigated for the removal of chromium, that of precipitation at an elevated pH obtained by treating the solution with nickel carbonate, proved satisfactory. Figure 11 shows the effect of pH on the trivalent chromium concentration in the four types of solutions. In Figure 12, the effect of temperature is illustrated. It was found that the chromium concentration could be reduced to a level of 5 mg./l. or less with no loss of nickel at a pH level which is readily reached, i.e., 5.2 - 5.5. The higher the temperature at which the precipitation takes place, the more rapid and complete is the removal. To insure as complete a removal as possible, the solution should be held at a high temperature for several hours, and then allowed to stand at room temperature for twelve to twenty four hours.

The precipitation method is satisfactory only for chromium in the trivalent state. Any hexavalent chromium present in solution is unaffected at pH values of 5.8 and higher. To remove the hexavalent chromium economically, it must be reduced and then precipitated. This reduction may be accomplished chemically, e.g., using sulfur dioxide or sulfurous acid in a low pH solution, or electrochemically. The first method involves adjusting the pH and after the reduction is complete, removal of the excess SO_2 by heating for example. The electrolytic reduction requires more time and means loss of nickel by deposition. A second method of chemical reduction, and perhaps the easiest, is to reduce the chromium with nickel metal. A low pH (below 3.0) and agitation are required for efficient results. Considerable time is needed for this method but the least amount of solution treatment and handling is involved.

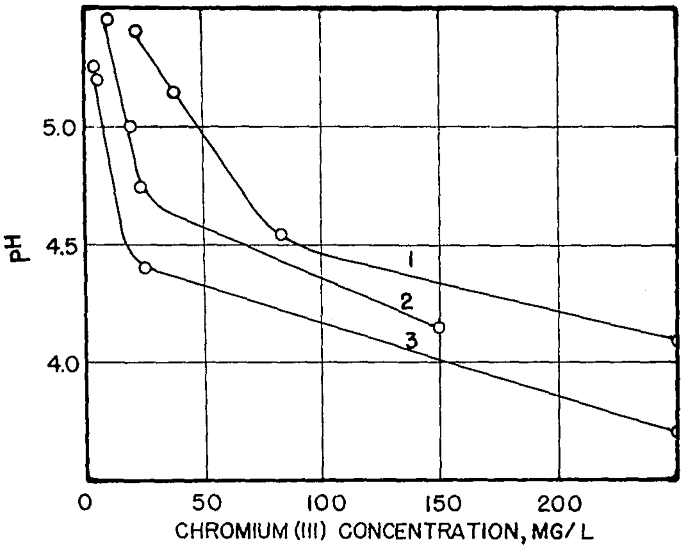

FIG. 11 REMOVAL OF CHROMIUM (III) FROM NICKEL PLATING SOLUTIONS BY HIGH-pH PRECIPITATION

1. NICKEL-COBALT ALLOY TYPE SOLUTION
2. ORGANIC TYPE SOLUTION
3. WATTS TYPE SOLUTION

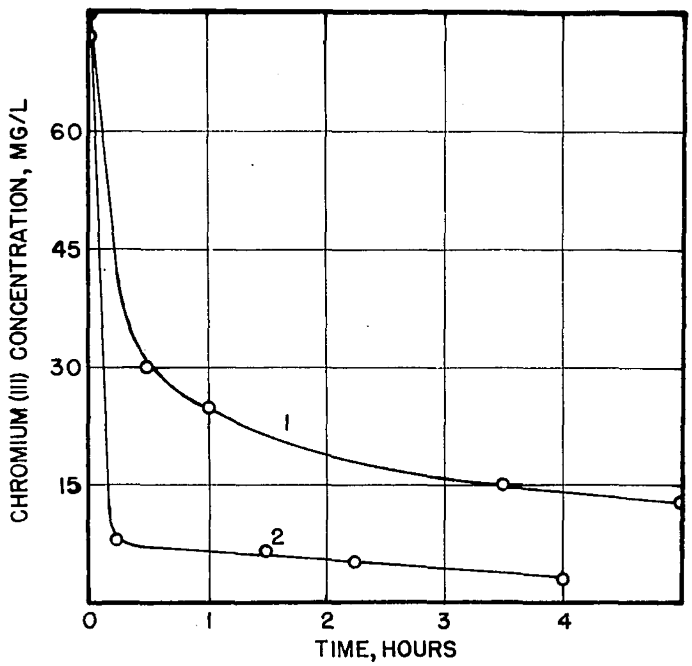

FIG.12 EFFECT OF TEMPERATURE AND TIME ON THE COMPLETENESS OF THE REMOVAL OF CHROMIUM (III) BY HIGH-pH TREATMENT

1. 55° C.
2. 75° C.

SUMMARY

The results of this investigation of the effects of varying concentrations of trivalent and/or hexavalent chromium dissolved in nickel solutions may be summarized briefly as follows:

The concentration of trivalent chromium affect the maximum amount of hexavalent chromium that could be present and vice versa: the more trivalent chromium in solution, the lower the concentration of hexavalent chromium must be, the converse also being true. When both were present, their combined effect was greater than when either was present alone.

The effect on appearance of chromium in either the hexavalent or trivalent state was not pronounced. In the Watts pH 2.2 solution the presence of trivalent chromium in excess of 25 mg./l. produced a smoother, finer grained deposit. When hexavalent chromium was present in concentrations varying from 15 - 75 mg./l. the deposits were whiter, but not noticeably smoother or finer grained. Trivalent chromium started to precipitate in the Watts 5.2 solution almost immediately when trivalent or hexavalent chromium was the initial impurity. Roughness appeared in both cases. The hexavalent chromium produced a whiter deposit than a pure solution, an effect not noticed when trivalent chromium only was present. Chromium in both valence states produced stress in the nickel-cobalt deposits but otherwise had no effect. Its effect on deposits from the organic nickel solution was to cause a slight milkiness when

present in the trivalent state in sufficient concentration (125 mg./l. or more). Hexavalent chromium had little effect on the deposits from the organic type solution containing up to 20 mg./l.

No discernible change in the adhesion of the deposits to the base metal was noted in the specimens from any of the solutions containing either hexavalent or trivalent chromium within the concentration ranges studied as long as careful control of conditions during deposition was maintained.

The ductility of the deposits from all four types of solutions was noticeably decreased when trivalent or hexavalent chromium was present in solution. The decrease was, in general, more pronounced when hexavalent chromium was the impurity than when trivalent chromium was the sole contaminant.

In general, the salt spray corrosion resistance of the deposits from the four types of solution decreased as the trivalent chromium content increased. The maximum decrease was of the order of twenty five percent. Hexavalent chromium seemed to have little effect on this property. Its effect was to increase corrosion resistance in some cases, i.e., Watts pH 2.2 and decrease it slightly in others, i.e., organic and nickel-cobalt. The deposits from the Watts pH 5.2 solution showed both increase and decrease in this property. The hexavalent chromium appeared to override the effect of trivalent chromium to reduce corrosion resistance. The concentration of trivalent chromium had an effect here also. The higher the concentration of trivalent chromium in the presence of hexavalent chromium, the lower was the salt spray resistance.

The efficiency of the solutions was unimpaired by the presence of trivalent and/or hexavalent chromium. The effect of trivalent chromium was to increase slightly the throwing power of the two Watts type solutions and the organic type solution. A slight decrease in this property was noted with the nickel-cobalt type solution. Hexavalent chromium increased the throwing power of the organic and Watts pH 5.2 solution and decreased the throwing power of the nickel-cobalt and Watts pH 2.2 solutions.

The concentration of chromium may be reduced to 5 mg./l. or less by high pH precipitation using nickel carbonate. Maintaining the solution at a temperature of 75° C. or higher, apprediably increases the rate of removal. Allowing the solution to stand at room temperature for several hours after heating makes the removal more complete. This method is satisfactory for hexavalent chromium if the chromium (VI) is reduced to the trivalent state first by electrolytic or chemical means. For the latter, nickel metal in a solution of low pH with agitation works well.

Electrolytic removal of chromium at current densities below 40 a.s.f. either from the hexavalent state or the trivalent state is unsatisfactory. The trivalent chromium is removed very slowly if at all and the hexavalent chromium, although it is deposited at high current densities, is reduced to trivalent faster than it is removed.

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