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UNIVERSITY OF LOUISVILLE

THE ELECTRODEPOSITION OF CHROMIUM-NICKEL ALLOYS

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

RICHARD JAMES WHELAN, JR.

Year

1952

16 June '33 M.P.S.

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INTRODUCTION

Chrome-nickel alloys and steels have of recent years been produced commercially. They have the properties of withstanding extreme conditions of temperature, pressure, and chemical corrosion. This investigation was undertaken with the idea of producing electrodeposited alloys of nickel and chromium on iron and other base metals. These deposited alloys should produce a non-porous surface which would be capable of withstanding the deleterious effects of fumes, vapors and chemicals which cause destruction of nickel and chromium deposits. The alloy should have the additional properties of hardness and abrasion resistance.

It has not been considered possible to deposit alloys of nickel and chromium, because nickel has been deposited from neutral or slightly acid solutions, while chromium is deposited from distinctly acid solutions.

It is only of recent years that chromium has been successfully electrodeposited commercially, yielding a surface highly resistant to atmospheric corrosion and also having characteristics of extreme hardness.

The disadvantage encountered in electrodeposited chromium is porosity, and an intermediate layer of some metal which will protect the underlying surface from corrosion is therefore necessary. Successful chromium deposits have been made over intermediate coats of copper and nickel on the base metal iron.

An electrodeposited nickel surface presents a high luster, similar in reflecting quality to silver and at the same time acts as a protective coating for iron or steel. It is extensively used for ornamental purposes. The corrosion resisting properties of nickel depend on the impervious quality of the surface which should be .001" thick in order to protect steel.

Alloys having chromium as one constituent tend to resist the corrosive action of gases and liquids, unless these alloys contain a large percentage of another metal easily attacked by the corrosive agent. The purpose of the electrodeposition of an alloy of chromium-nickel directly on the iron or copper base is to reduce the porosity, while at the same time retaining the corrosion-resisting qualities of chromium. In this manner, moisture and destructive acids may be prevented from penetrating the outer surface and attacking the underlying metal.

Each of these metals has been co-deposited with other metals, but not with each other. A number of nickel alloys have been electrodeposited, among them being, nickel-copper (1), nickel-tin (2), nickel-iron (3), nickel-cobalt (4), and nickel-zinc (5).

In all cases except the last mentioned, the metal content of the deposits varies with the ratio of metals in solution, when the current density is high. Nickel-zinc alloys are unique, in that, although the solution contains an excess of nickel, the deposit contains more zinc than nickel.

Nickel and iron were simultaneously deposited by Leuchter (6) from NiSO_4 and FeSO_4 , using the latter in excess.

Nickel has been deposited simultaneously with other metals in the form of the ternary alloys, Cu-Ni-Zn (7), Cu-Ni-Sn (8), and Fe-Ni-Co (9).

Experimenting on chromium-iron alloys, Fuseya and Sasaki (10) found that chromic acid and iron salts resulted in a poor deposit, and therefore, they used a bath composed of the mixed sulfates, to which was added an excess of sulfuric acid. It was found that by increasing the current density and lowering the temperature, the percentage of chromium was increased.

Siemens and Halske (11) have patented a process by which nickel and chromium can be simultaneously deposited from a molten bath composed of chromic oxide (15 parts), borax (40 parts), sodium metaphosphate (50 parts) and the addition of a nickel salt. The temperature is 950° C. and the current density about 1000 amps./sq. m. of cathode surface.

In 1905, the first electrodeposition of chromium was carried out by Carveth and Curry (12), who showed that the reduction of chromic acid (CrO_3) at a high current density yielded metallic chromium, and that salts, such as sulfates, improved the character of the plate. The first bath to arouse commercial interest was that of Sargent (13) in 1920, and it is essentially the same as that used in modern plating. The commonly used bath for chromium deposition is composed of 2.5 M CrO_3 and about 2.5 gms. of $\text{Cr}_2(\text{SO}_4)_3$ per liter, using a cathode current density of 12-40 amps./sq. dm. and lead anodes. Schneidewind summarizes the existing patents dealing with chromium deposition and states that no single patent or group of patents can control the deposition of chromium from chromic acid baths (14).

The first commercial attempt to deposit nickel electrolytically, was made by Adams (15) in 1865, employing a solution of NiCl_2 and anodes of cast nickel.

At present, the standard bath for commercial nickel deposition is composed of the single salt, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ added to increase anode corrosion and H_3BO_3 to regulate the acidity. Anodes of cast nickel or electrolytic nickel are used, and these dissolve with high anode efficiency in the presence of chlorides.

THEORETICAL

Two metals can be simultaneously electrodeposited, provided the electrode potentials of these two metals in contact with solutions of their ions are the same.

The normal electrode potentials of nickel, chromium, and hydrogen are shown in Table I. (16)

TABLE I

NORMAL ELECTRODE POTENTIALS			
	Hydrogen	N. Calomel	Absolute
Cr	-0.47	-0.75	-0.19
Ni	-0.20	-0.48	0.08
H ₂	0.00	-0.283	0.277

The Nernst formula for the determination of the electrode potential is derived from the concept of osmotic and solution pressures. The osmotic pressure is the pressure exerted by the metal ions, or their tendency to pass from the ionic to the atomic state; and the solution pressure is the tendency of the metal to dissolve or to pass from the atomic to the ionic state.

$$E = \frac{RT}{nF} \ln \frac{kC}{P} \quad (1)$$

Where the solution is normal with reference to the particular ions, the equation becomes

$$E_0 = - \frac{RT}{nF} \ln \frac{P}{k}$$

Subtracting, we obtain

$$E_0 = E - \frac{RT}{nF} \ln C.$$

E = single electrode potential

E_0 = normal electrode potential

R = gas constant

T = absolute temperature

n = valence of the metal

F = Faraday constant (96,540 coulombs)

P = electrolytic solution pressure

k = proportionality constant

C = molar ionic concentration

If the two metals are to deposit simultaneously, the values of E for both must be the same. The electrode potential is a function of many complex variables. It is affected by concentration, current density, overvoltage, polarization, temperature and cathodic alloy formation.

EFFECT OF CONCENTRATION

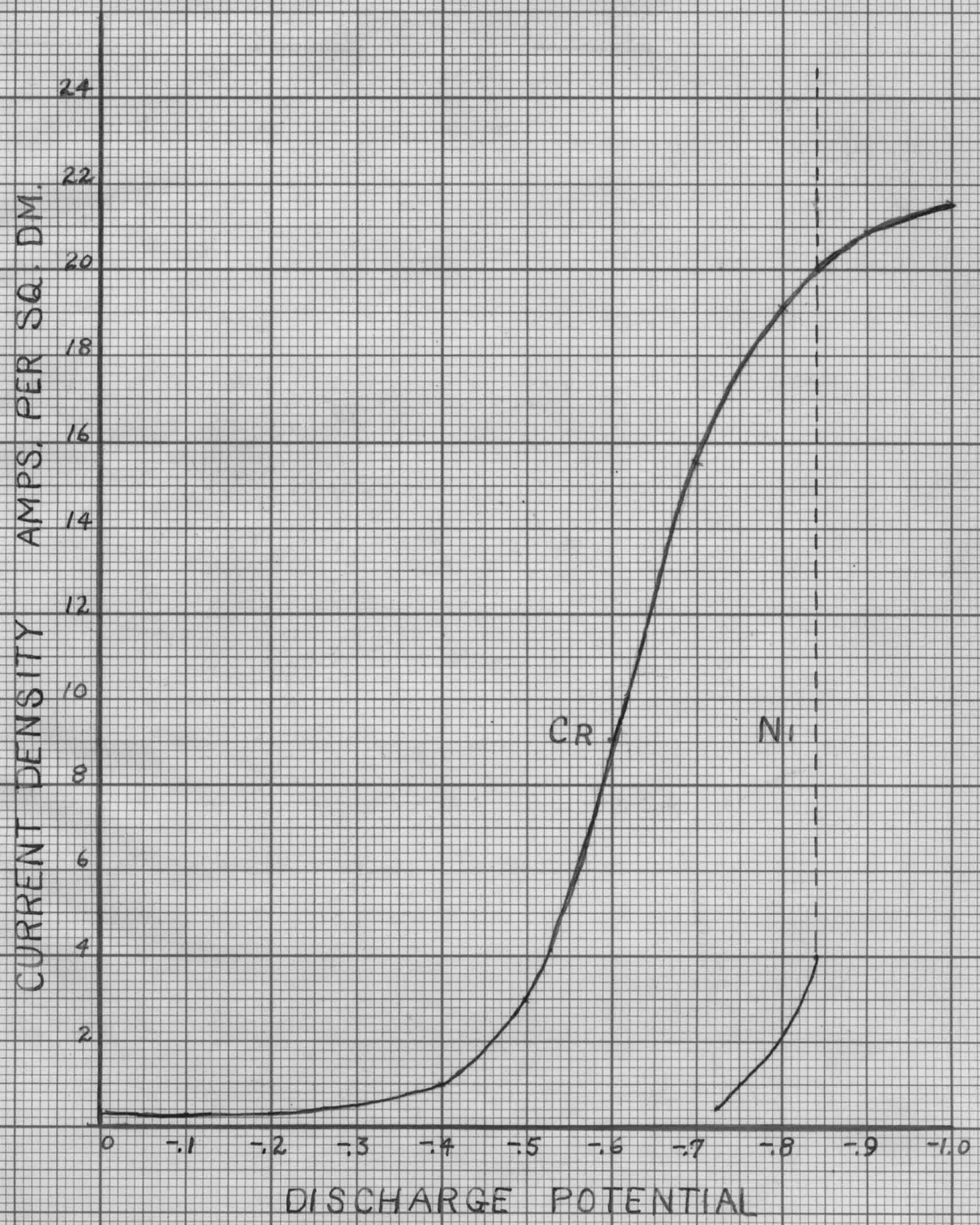
According to equation (1), the single potential of a metal will vary with concentration. Dilution and the formation of complex salts both affect the ionic concentration. Dilution is not recommended in nickel-chromium deposition, since both metals are normally deposited from solutions of high metal salt content. The metal ion concentration is greatly

reduced by use of complex salts, and at the high current densities necessary for satisfactory chromium deposition, the solution would rapidly become impoverished in chromium ions.

The sodium or potassium chromium cyanides are unknown and therefore, cyanides as complexes are not considered practical, although $\text{Ni}(\text{CN})_2$ exists. The corresponding complex salts of these metals are not common; and while chromates and dichromates are common, the corresponding nickel salts are unknown. Variation of concentration by dilution and complex ion formation are not therefore practical methods of bringing the potentials together.

By increasing the current density, the potentials of two metals can be made to approach each other; and hence, since the difference between the single electrode potentials of Ni (-0.20) and Cr (-0.47) is only 0.27 volts, these potentials should become equal at higher current densities. The current density-potential curves are given in Fig. I. The values for chromium (17) show that at high current densities, the curve bends distinctly to the right. The curve for nickel (18), while only available for low current densities, because experimental work has been carried on only at these low

FIG. I
CURRENT DENSITY - DISCHARGE POTENTIAL
CURVES



EUGENE DIETZGEN CO.
Chicago and New York

EDCO Efficiency
20 X 20

N° 340-

current densities, shows that if the values are extrapolated, the curves cross at about 20 amps./sq. dm. This would lead one to expect that at high current densities, the two metals might be simultaneously deposited.

EFFECT OF CURRENT DENSITY

There is wide variance in the effect of current density on the two metals. In NiSO_4 solutions, an increased current density causes a greater electron flow, resulting in a more rapid deposition of nickel. In CrO_3 solutions, a low current density merely effects a partial reduction of Cr^{VI} to Cr^{III} , but does not complete the reduction to the metallic state. It is only when the current density exceeds a point at which the discharge potential of chromium becomes equal to that of hydrogen that metal is deposited.

This variable, current density, is not so important in nickel deposition, for a good deposit can be obtained from 0.5 - 10.0 amps./sq. dm., and, the temperature being held constant, an increase in current density will give finer grained deposits, since new nuclei are formed more rapidly, and those already formed have no period of growth. Being more electro-negative than hydrogen and also being deposited from

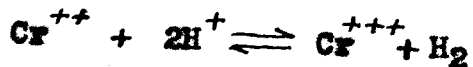
an acid solution, hydrogen is evolved with the nickel which tends to give a fine-grained, though brittle plate.

Schneidewind (19) shows that increased current density results in increased current efficiency for several ratios of $\text{Cr}^{\text{VI}}/\text{SO}_4$, and his results show that the range for bright chromium deposits is widened as the current density increases. Current density has an effect on the formation of Cr^{III} , the maximum amount of which is formed at low current densities. The type of material used as cathode has an effect on Cr^{III} as studied by Lukens (20), who found that nickel as cathode material formed the least amount of Cr^{III} , copper more, and lead the largest amount.

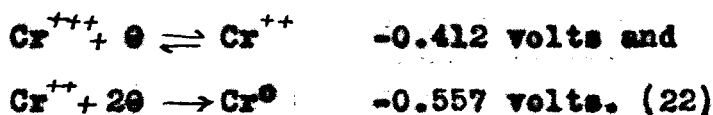
The reaction in the separate deposition of nickel and chromium is as follows:



or, in other words, the deposition of either metal depends on the presence of bivalent ions. In the case of nickel, the bivalent ions are present in the solution of NiSO_4 , while in CrO_3 , the hexavalent ions must be reduced to the bivalent state. Liebreich (21) assumes the existence of an equilibrium



and uses this hypothesis to explain the evolution of hydrogen with the reduction of valence. The potentials of the two processes are



According to Sargent (23), deposition of chromium from $\text{CrO}_3 - \text{Cr}_2(\text{SO}_4)_3$ solutions at moderate current densities, is accompanied first by the formation of a film on the cathode with a nearly neutral solution in contact with it; while at higher current densities, a film forms and hydrogen is evolved.

In general, at high current densities, one would expect the possibility of simultaneous deposition of chromium and nickel. The efficiency, due to the evolution of hydrogen, would be low, and the resulting deposits may be brittle, due to adsorbed hydrogen. Increased current densities would increase the chromium content to a value where the current density-discharge potential curves cross each other, and above that point one would expect an increased amount of nickel in the deposit.

HYDROGEN DISCHARGE AND OVERVOLTAGE

Table I shows that both nickel and chromium are 0.2 and 0.47 volts respectively, above hydrogen in the electrochemical series, and when the deposition is

carried out from solutions, normal with respect to metal ions, there is a preferential discharge of hydrogen, since a lower potential is required to deposit hydrogen than is necessary to deposit either metal. Therefore, gassing occurs simultaneously with the deposition of either metal. This large volume of hydrogen, which requires considerable energy, causes a low cathode efficiency for deposition.

Nickel can be deposited from solutions of low pH; namely, below 3.0, using higher current densities than with solutions of commonly used pH (5.5). The increased acid aids anode corrosion but lowers the current efficiency to about 75% due to large amounts of hydrogen being discharged (24).

The overvoltages of the two metals are given in Table II (25). These hydrogen overvoltages were measured in 2 N. H_2SO_4 saturated with hydrogen.

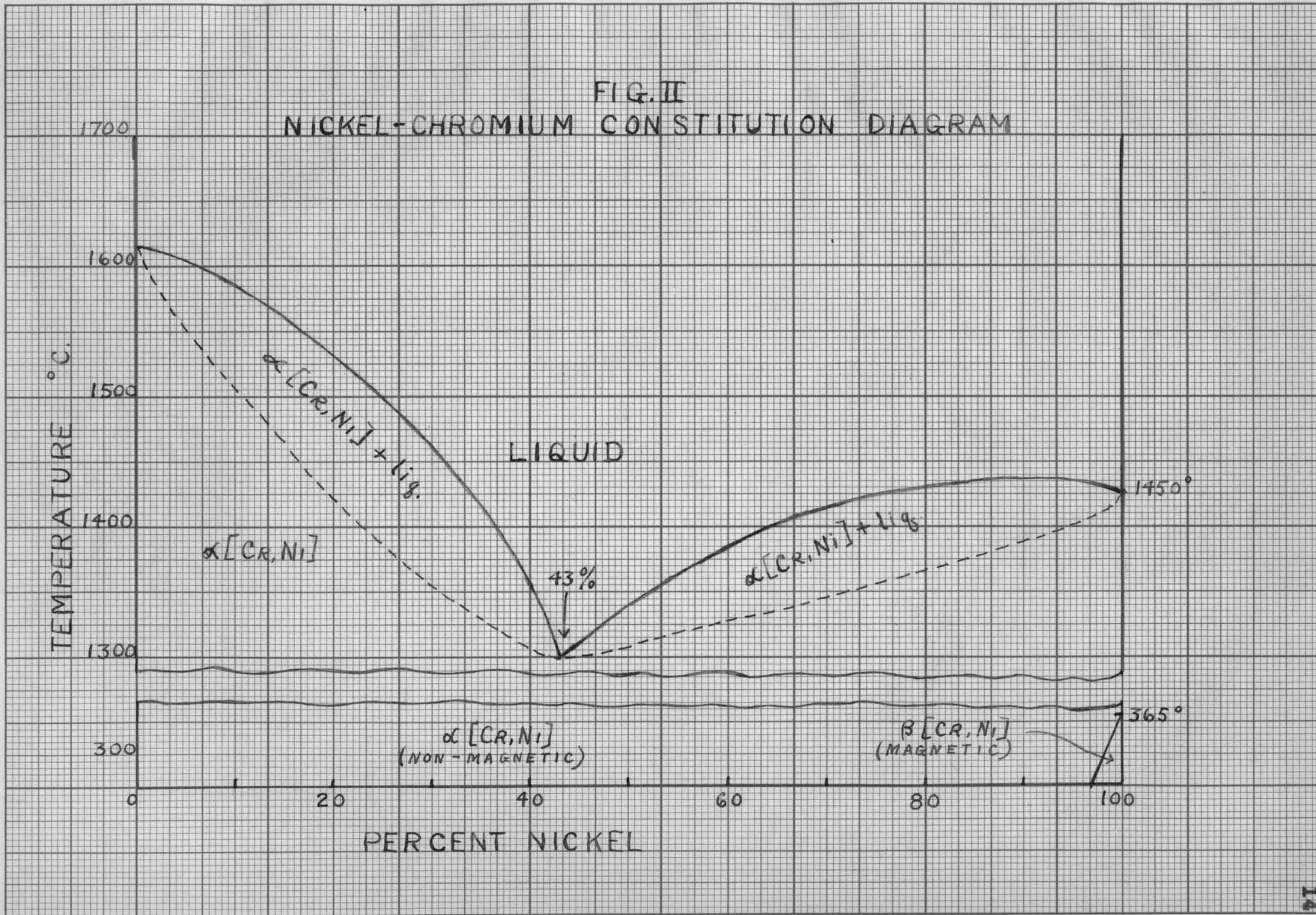
TABLE II

HYDROGEN OVERVOLTAGES AT 25° C.

C.D. in milliamps. per sq. cm.	Ni	Cr
1	0.563	0.32 x
10	0.747	
100	1.048	
1000	1.241	

x current density not given.

FIG. II
NICKEL-CHROMIUM CONSTITUTION DIAGRAM

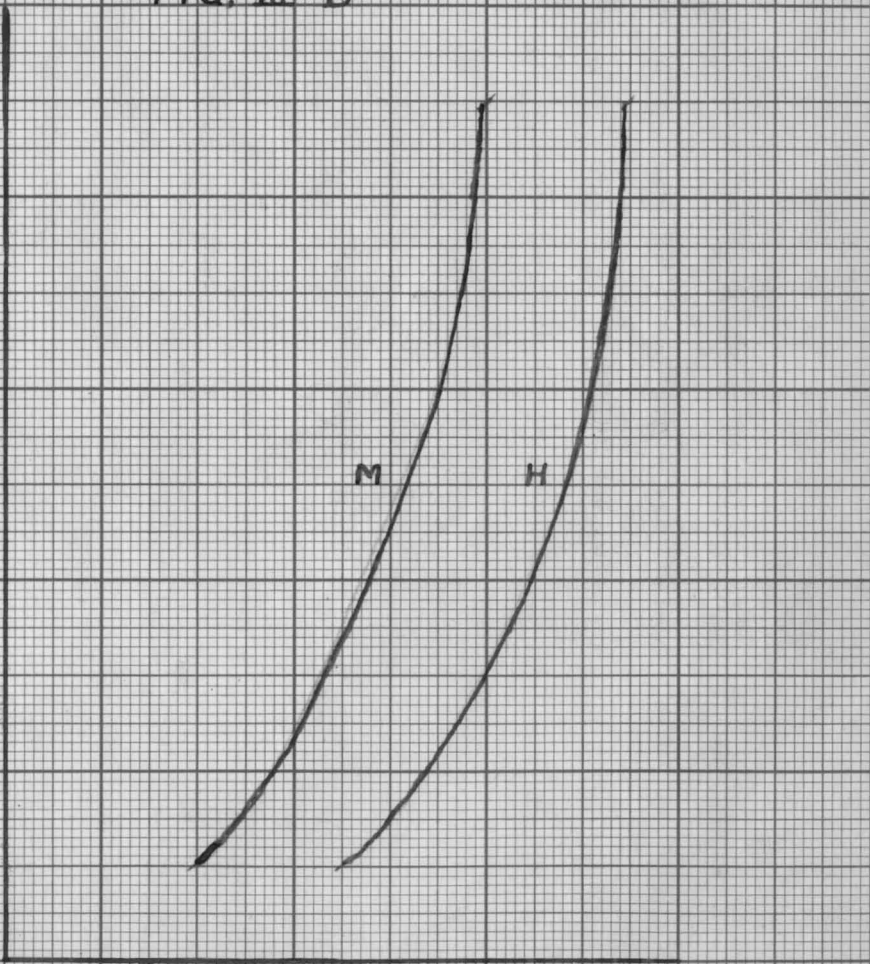
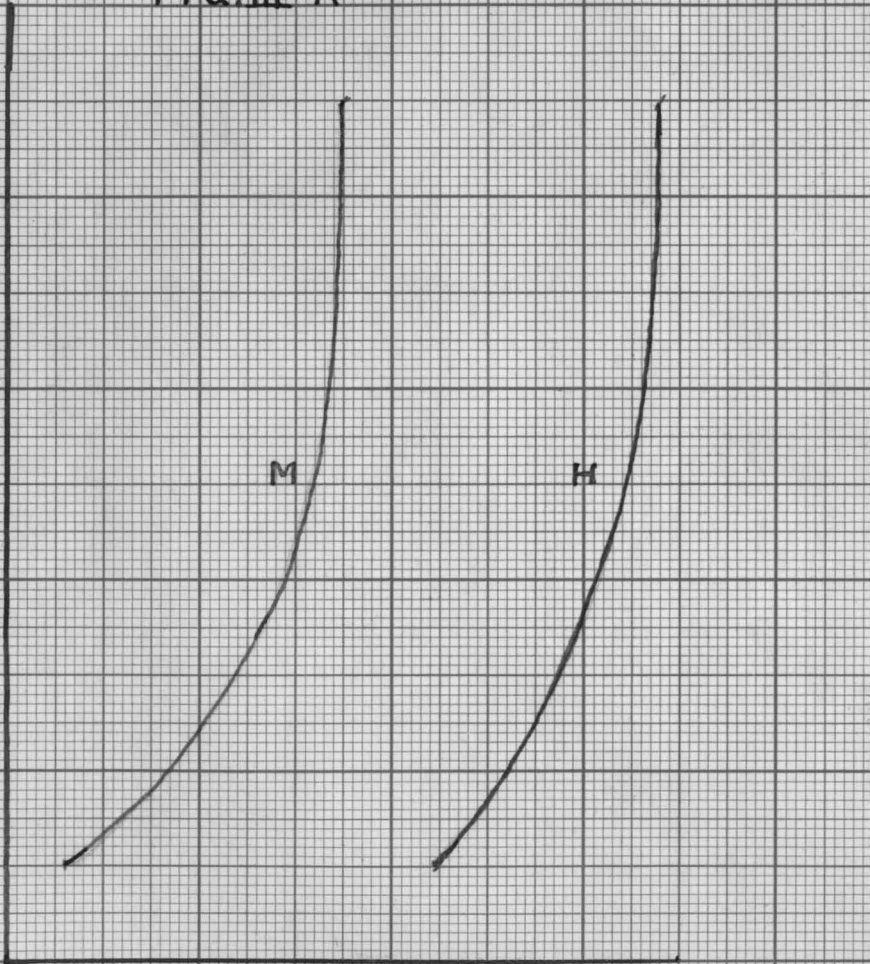


CURRENT DENSITY - POTENTIAL CURVES

FIG. III-A

FIG. III-B

CURRENT DENSITY



POTENTIAL

CONDITIONS FOR DEPOSITION OF METAL

POTENTIAL

CONDITIONS FOR DEPOSITION OF METAL AND HYDROGEN

These values show that for nickel the overvoltage increases with current density. No values are available for overvoltages of nickel-chromium alloys; but since the constitution diagram (Fig. II) (31) indicates that these metals form a series of solid solutions, the overvoltage of the alloy is probably intermediate between that of nickel and that of chromium.

These values for overvoltage would indicate that there is a possibility of depositing nickel from a bath of low pH and the simultaneous deposition of the two metals would be possible, even though it is accompanied by a co-deposition of hydrogen.

Before hydrogen will be discharged from a solution, an electromotive force must be impressed which exceeds the hydrogen overvoltage of the metal. Whether a metal, hydrogen, or both will be deposited, depends on the values of E_M and E_H as determined by Equation I, where E_M is the single electrode potential for the metal, and E_H is the single electrode potential for hydrogen. If E_M is less electronegative than E_H , only metal will deposit, as in Fig. III-A. If E_M is more electronegative than E_H , only hydrogen will be liberated, except where E_H plus the overvoltage is greater than E_M .

In Fig. III-B (26) the overvoltage of the metal for a given current density, is equal to that of the

hydrogen; and hence, the two will deposit together. Now it is also possible to obtain the same relationship for two metals, and in this manner form an alloy of these metals.

POLARIZATION

Polarization may be defined as a counter electromotive force caused by the depletion of substances used in the reaction, faster than they can be replaced, or the formation of the products of the reaction faster than they can be removed.

The rate of depletion of ions in the region of the cathode varies with the current density, resulting in an increase in polarization, thus requiring a greater potential to obtain the desired current. The current density-discharge potential curves (Fig. I) show that the curve for nickel at high current densities is less electronegative than the chromium curve, and one would expect the deposition of nickel from these potential curves alone, even though there were no depolarizing action. By depolarizing one of the metals, the discharge potential of the other metal is made nearly equal to that of the depolarized metal. This depolarization causes the formation of an alloy and the two metals are present either as a

compound or a solid solution. (27) The potential of a metal in a solution of its ions changes with the concentration of these ions, and the potential increases as the solution becomes more dilute; but this change is not a direct function of the concentration change. If chromium is depolarized by nickel, there is a possibility of simultaneous deposition at a lower potential.

The constitution diagram for chromium-nickel alloys (Fig. II) shows that nickel and chromium form a complete series of solid solutions with a minimum. The potential for varying composition of the alloy would therefore be intermediate between those of the two metals, and simultaneous deposition would be expected.

EFFECT OF ANODES

In the deposition of most metals, anodes of the respective metals are used in alloy deposition. It is customary to use anodes of each metal or cast anodes of the alloy in the ratio desired. For practical alloy deposition, the composition of the bath must remain constant; and consequently, an anode of the two metals is necessary, such that the metals will dissolve in the same ratio as they are removed from solution.

In chromium deposition, various anodes have been investigated (28). Nickel and iron anodes become passive in oxidizing solutions. Chromium in steel renders it unfit for anode use, since it is too easily oxidized in the CrO_3 solution. Ferro-chromium and Ni-Cr alloys (Chromel, Nichrome, etc.) are worthless as anodes.

In nickel deposition, pure electrolytic nickel becomes passive and much better results are obtained by using cast anodes with a small amount of impurities. In order to aid anode corrosion, a soluble chloride is added; preferably $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, since it has the advantage of adding a common ion thus repressing the (SO_4^{--}) ; which, in case of the mixed bath of $\text{NiSO}_4 - \text{CrO}_3$, is in excess of the preferable ratio of $\text{Cr}^{\text{VI}}/\text{SO}_4$ of 50-1 as recommended by Schneidewind. (19)

Lead anodes for chromium plating are less soluble at low temperatures but more soluble at high temperatures than iron. Schwartz (29) favored the use of chromium or ferro-chromium anodes but Watts (28) found the anode efficiency was greater than the cathode efficiency. The earliest records of chromium deposition reveal that platinum anodes were used. Placet and Bonnet (30) were the first to mention the

use of lead anodes. The theory, as held by several authors, of the usefulness of lead anodes for the oxidation of Cr^{III} to Cr^{VI} , is that either a chromate or an oxide is formed on the lead, and this oxidizes the trivalent chromium to the hexavalent state.

Since lead is not used to supply metal ions, the passivity is very favorable to oxidation and the maintenance of equilibrium between Cr^{III} and Cr^{VI} .

If the anode efficiency is low, the cathode efficiency of the nickel bath is decreased, due to increased acidity; but this theory does not apply under the conditions of this investigation in which insoluble lead anodes were used.

CONCLUSION

Chromium and nickel have not been previously electrodeposited simultaneously from aqueous solutions. Chromium is usually deposited from a bath of a low pH; while nickel is deposited from a bath with a pH of about 5.5.

It should be possible, however, to deposit these metals from an acid solution, using a high current density; as the overvoltage increases with current density, and the current density-discharge potential curves for nickel and chromium cross at high current densities. The efficiency of deposition of the nickel-chromium alloy from an acid solution would be low, due to hydrogen evolution.

EXPERIMENTAL

PRELIMINARY EXPERIMENTAL

The purpose of this investigation was to attempt the simultaneous deposition of alloys of nickel and chromium from aqueous solutions. There has been no previous work reported on this alloy, and the experimental work resolved itself into a study of (1) a suitable bath for deposition and (2) the best operating conditions.

Chromium, as previously mentioned, has been plated from chromic acid solutions, but the electrodeposition of nickel has been limited to solutions of a pH of 5, except in one case mentioned. Thus, previous work suggested the impracticability of simultaneous deposition.

Binary and ternary alloys have been successfully deposited from cyanide solutions and these solutions suggested themselves for deposition of nickel-chromium alloys.

Nickel cyanide was prepared when nickel chloride was treated with a concentrated solution of KOH and excess KCN. It was found impossible to prepare a double sodium or potassium chromium cyanide. When KCN was added to CrCl_3 , cyanogen was evolved; but when made alkaline, $\text{Cr}(\text{OH})_3$

was precipitated and was not soluble in excess KCN. Various other unsuccessful methods of preparing the complex potassium chromium cyanide were tried and deposition from cyanide solutions was abandoned.

A standard nickel plating bath to which were added various chromium salts, was next tried. K_2CrO_4 and $Cr_2(SO_4)_3$ were added as the chromium salts.

The concentration of the combined baths was:

$NiSO_4 \cdot 6H_2O$	_____	140 gm./l.
K_2CrO_4	_____	120 gm./l.
$Cr_2(SO_4)_3$	_____	5 gm./l.

This solution was made acid with H_2SO_4 , heated to $60^\circ C.$ and operated at 3 volts and 12.5 amp./sq.dm., using Cu cathodes and Pb anodes. The resulting deposit was a dull grey. Further experiments using this bath under varying conditions did not give satisfactory results, as no chromium was found in the deposit.

Nickel can be successfully deposited from a solution of $NiSO_4$ and $NiCl_2$, and chromium is commercially deposited from a solution of CrO_3 ; therefore, the alloy should, under proper control of conditions, be deposited from a mixed bath. A bath containing the combination was prepared using the following concentrations:

CrO_3	_____	250 gm./l.
$NiSO_4 \cdot 6H_2O$	_____	250 gm./l.
$NiCl_2 \cdot 6H_2O$	_____	15 gm./l.

By using this solution at 15 amp./sq.dm., a black deposit was obtained which gave qualitative tests for both nickel and chromium. This bath indicated that the two metals could be simultaneously deposited from an acid bath. The remainder of the work was done, using this bath and varying the concentrations and operating conditions.

MATERIALS AND APPARATUS

Stock solutions were prepared containing NiSO_4 - NiCl_2 and CrO_3 in concentrations greater than any which were to be used in the investigation. The nickel bath contained NiSO_4 - 500 gm./l. and NiCl_2 - 30 gm./l. and the chromium bath contained CrO_3 - 500 gm./l.

The NiSO_4 was prepared by recrystallizing a solution of technical NiSO_4 , and the NiCl_2 was prepared by the action of concentrated HCl on C. P. NiCO_3 . After action had ceased, the solution was evaporated to dryness, dissolved and recrystallized to remove the excess HCl , which would tend to make the mixed plating bath more acid.

The plating solutions were analyzed separately to determine the metal content. The chromium analysis was made volumetrically by using KI and titrating the

excess iodine with $N/10$ $Na_2S_2O_3$. The nickel solution was determined by the potassium cyanide method. These methods were carried out as directed by "Scott's Technical Methods of Analysis". The analyses showed:

Nickel _ _ _ _ _ 54.9 gm./l.

Chromium _ _ _ _ _ 210.4 gm./l.

An attempt to determine the pH of the plating bath by electrometric titration, using the quinhydrone electrode, proved unsuccessful since the strong concentration of chromic acid decomposed the quinhydrone. Indicators were not held practical, due to the dark red color of the solution, which would easily mask any color change in the indicator.

The solutions used during the investigation contained the following concentrations:

TABLE III

SUMMARY OF COMPOSITION OF ELECTROLYSIS BATHS

Bath No.	Concentration in grams per liter					Ratio Cr:Ni
	CrO ₃	H ₂ SO ₄	NiCl ₂	Cr	Ni	
1	250	250	15	105.23	27.45	3.83
2	200	200	12	84.18	21.96	3.83
3	166	166	10	69.45	18.12	3.83
4	125	125	7.5	52.61	13.73	3.83
5	125	245	7.5	52.61	26.81	1.96
6	156	245	7.5	65.66	26.81	2.45

The above solutions were used as a basis to which were added varying amounts of acid, base and addition agents.

The method of analysis of the deposits consisted in dissolving the alloy in concentrated HCl and dividing the solution into two portions, one of which was tested for nickel, the other for chromium.

The qualitative method used for nickel thruout the investigation was to make the solution alkaline with NH_4OH and add a few drops of di-methyl glyoxime. When heated, a red precipitate gave an identification for nickel. The detection of chromium required the oxidation of Cr^{+++} to Cr^{+++++} . The solution was made alkaline with 2.5N NaOH, Na_2O_2 was added and the solution boiled until a clear yellow color appeared. Acetic acid was added and a yellow precipitate with barium acetate or barium chloride, in an excess of acetic acid, showed the presence of chromium. Copper and steel cathodes were generally employed, and being soluble in HCl, the solution contained not only the deposit but part of the base metal which interfered with the detection. It was necessary to remove the foreign metal before the qualitative test was made.

The solution was electrolyzed in a crystallizing dish (10 cm. in diameter) but beakers were used later. In order to accommodate two and sometimes four anodes

a 1000 c.c. beaker was used; but when small volumes of solution and one anode were being used, 400-600 c.c. beakers were satisfactory.

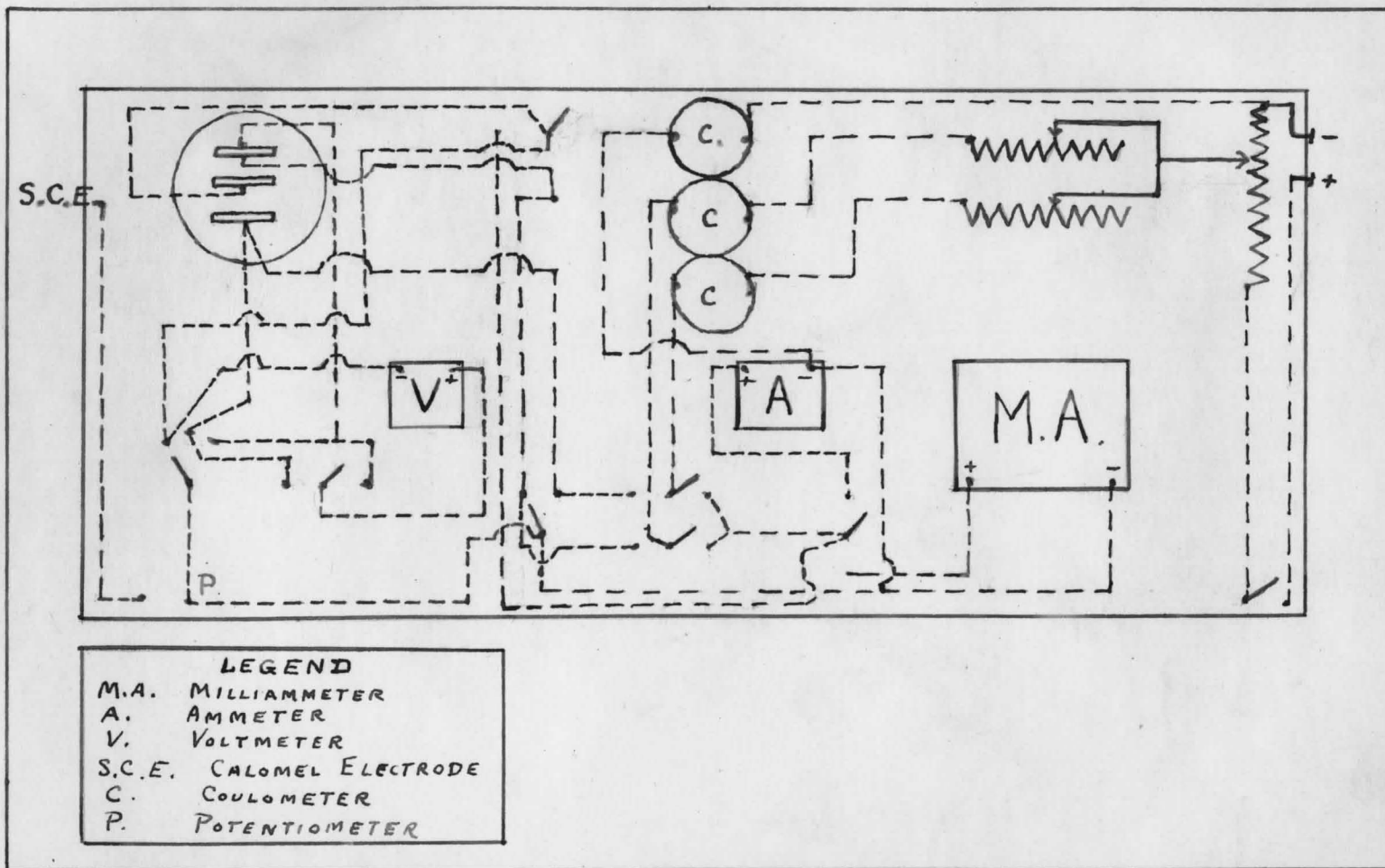
The anodes were of lead approximately 16 sq.cm. in area; and the steel, copper and platinum cathodes were approximately 25 sq.cm. in area. The same area of anode and cathode surface; that is, about 0.1 sq.dm., was immersed in the solution, in order to maintain equal current densities on both.

An instrument board (Fig. IV) gave complete control of the current thru the anodes and cathode and the IR drop across the bath. The instrument board was provided with coulometers for measuring the current efficiency and a potentiometer for determining anode and cathode polarization. These properties were not studied, as the preliminary nature of the work did not justify these determinations. Their further study, however, is recommended.

FINAL EXPERIMENTAL

Preliminary experimental work showed that an alloy of chromium-nickel could be electrodeposited from a solution containing: CrO_3 - 250 gm./l., NiSO_4 - 250 gm./l., and NiCl_2 - 15 gm./l., using a

FIG. IV
 DIAGRAM OF SWITCHBOARD



lead anode and a copper cathode, operating at 15 amp./sq.dm. and 60° C. bath temperature. Electrolysis baths of the composition given in Table III were used. The time of the electrolysis was one hour, unless otherwise noted.

Bath I, containing 250 gm./l. CrO₃, 250 gm./l. NiSO₄, and 15 gm./l. NiCl₂, was operated at 25-27° C. under varying conditions of current density.

TABLE IV

EFFECT OF CATHODE MATERIALS ON BATH I

Current Density amp/dm ² .	Cathode	Deposit
5.0	lead	chromium
10.0	lead	chromium-nickel
4.0	iron	nickel
5.3	iron	nickel
6.8	iron	nickel
8.3	iron	nickel

Using lead cathodes, Cr was deposited; but the deposit was not adherent and very coarse. Iron cathodes were used to obtain a brighter surface on the base metal, and only nickel was deposited.

The same solution was now neutralized with NaOH and the bath temperature elevated to 60° C. The results are shown in Table V.

TABLE V

EFFECT OF CURRENT DENSITY ON BATH I
AFTER NEUTRALIZATION WITH NaOH

Current Density amp/dm ² .	Cathode	Deposit
15.0	Pt	chromium-nickel
20.0	Pt	chromium-nickel
25.0	Pt	chromium-nickel

Although the chromium-nickel alloy was obtained in this neutral solution, the deposit was very poor and coarse and was easily peeled from the platinum. These results show that if the acidity is decreased, Bath I gives deposits of the alloy of nickel and chromium, but the deposits were dull and rough. These rough deposits suggested that too high a concentration was being used, and Bath II was prepared.

This bath contained 200 gm./l. CrO₃, 200 gm./l. NiSO₄ and 12 gm./l. NiCl₂. It was operated at 30° C. and 15 amp./dm.² Sodium hydroxide was added in small increments, and Table VI gives the results.

These results show that chromium is not deposited from a solution too alkaline with NaOH. The character of the deposits was the best yet obtained, being bright and adherent, although the composition was not as desired.

TABLE VI
EFFECT OF NaOH ON BATH II

NaOH gm./l.	Cathode	Deposit
4.0	Cu	Bright in center. but grey at bottom. Chromium-nickel
8.0	Cu	Bright over surface, Nickel
12.0	Cu	Bright over surface, slightly dull at one edge. Nickel

An investigation was now made, using lower concentrations, Bath III, containing 166 gm./l. CrO_3 , 166 gm./l. NiSO_4 , 10 gm./l. NiCl_2 and NaOH to neutralize the excess acid. This bath gave good yields of chromium over the entire range studied, but nickel was only slight at low current densities, but increased at higher current densities and a higher temperature.

This would indicate that the chromium is being depolarized by the nickel and therefore the alloy is depositing at a lower current density than would be

expected from Fig. I. The results are shown in Table VII.

TABLE VII
EFFECT OF CURRENT DENSITY AND TEMPERATURE
ON BATH III

Current Density amp./cm ² .	Temp.	Cathode	Deposit
10	25°	Cu	Bright at top, dull grey at bottom and sides, Chromium
12	25°	Cu	Bright at top, dull on bottom and sides, Chromium-nickel
20	60°	Pt	Dull over surface, bright on back, Nickel-chromium

The character of the above deposits indicated that the solution was too concentrated, and for the next series of experiments, a more dilute solution, Bath IV was used. The contents of this bath were: 125 gm./l. CrO₃, 125 gm./l. NiSO₄, 7.5 gm./l. NiCl₂ and NaOH to neutralize the excess acid.

When a platinum cathode was used, nickel and chromium were deposited. The deposits were coarse and rough with considerable treeing. Table VIII shows that no deposit was obtained below 15 amp./sq. cm. Smoother deposits were obtained when copper cathodes were used; but only chromium was deposited. The material of the cathode determines whether chromium

or the alloy will be deposited.

TABLE VIII
EFFECT OF CURRENT DENSITY AND CATHODE
MATERIAL ON BATH IV

Current Density amp./cm ² .	Temp.	Cathode	Deposit
10	60°	Pt	No deposit
15	60°	Pt	Dark grey at bottom and edges; light and smooth in center, Chromium-nickel
20	60°	Pt	Large, loose crystals; dark and peeling, Chromium-slight nickel
12	30°	Cu	Bright at top, center and back; grey at edges, Chromium
15	30°	Cu	Bright at top, center and back; grey at edges, Chromium
12	60°	Cu	Bright, adherent on sides and center; Chromium

The same solution, Bath IV, containing 125 gm./l. CrO₃, 125 gm./l. NiSO₄, 7.5 gm./l. NiCl₂ and 10 gm./l. KOH to neutralize the excess acid, was next used to study the effect of temperature on the deposits. Copper cathodes were used and the solution was agitated. When the solution is neutralized, chromium and nickel

are deposited; while in acid solutions, only chromium is plated out at 12 amp./sq.dm. and a temperature of 25° C. It is seen from Table IX that when the temperature is lowered to 15° C., no deposit is obtained, and at 50° C. the deposit is brown and corroded.

TABLE IX
EFFECT OF TEMPERATURE ON BATH IV

Current Density amp./dm ² .	Temp.	Deposit
12	15°	Deposit at top; brown crust below,
12	25°	Bright at top; grey at sides and bottom, Chromium-nickel
12	50°	Brown, corroded deposit; non-metallic

In order to determine the effect of NaOH on the deposition of the alloy, 5 gm. increments of NaOH were added to Bath IV. Copper cathodes were used and the bath temperature was 30° C. Neither metal was deposited from the alkaline solution, containing more than 20 gm. NaOH /l. Using 10 gm./l. and a current density of 12 amp./sq.dm., the deposit was bright, except around the bottom and edges, where it was slightly grey. The nickel content was very low and sometimes lacking.

TABLE X
EFFECT OF NaOH ON BATH IV

NaOH gm./l.	Current Density amp/dm. ²	Deposit
5	15	Bright at top; coarse at sides and bottom, Chromium
10	12	Bright at top and center; slight grey deposit at bottom, Chromium-slight nickel
15	12	Dull over entire surface; Chromium-slight nickel
20	12	No deposit
25	15	No deposit

The same solution was used in the next set of experiments, except that 15 gm./l. HCl were added to bring the solution back to a neutral point. Bath IV now contained 125 gm./l. CrO₃, 125 gm./l. NiSO₄, 7.5 gm./l. NiCl₂, 25 gm./l. NaOH and 15 gm./l. HCl. Copper cathodes were used and the solution was agitated during operation.

The regulation of hydrogen ion concentration is very important in the deposition of the nickel-chromium alloy. It was found that the neutralized solution did not give constant results. When the

solution became slightly alkaline, during the course of deposition, a brown crust was the usual result; although in some cases, no deposit was formed. This was attributed to the formation of basic salts or $Cr(OH)_3$ at the cathode. When the solution was slightly acid, deposits of the alloy were obtained, but the surface was rough and peeling or a dull, coarse grey. It will be noted in Table XI that this bath does not remain constant at higher temperatures. At $45^\circ C.$ the deposits become brown, rough and uneven.

TABLE XI
EFFECT OF NEUTRALIZING EXCESS NaOH
IN BATH IV

Current Density amp/cm ² .	Temp.	Deposit
12	30°	Grey at sides and edges; bright and adherent in center, Chromium-nickel
15	30°	Dull grey, adherent, Nickel-slight chromium
20	30°	Dull grey in center; white on bottom and edges; adherent, Nickel-chromium
12	45°	Grey on sides and bottom; bright on top; adherent, Nickel-chromium
15	45°	Grey in center; brown on sides and bottom. Rough, uneven.

In order to determine whether the excess acid was the deterrent factor in the nickel deposition, a special experiment was made using Bath IV, operated under the same conditions as previously. A temperature of 30° C. was maintained in a water bath, and copper cathodes were used. HCl was added in increments up to 100 gm./l. and the solution was agitated.

TABLE XII

EFFECT OF HCl ON BATH IV AT VARIOUS CURRENT DENSITIES

HCl gm./l.	Current Density amp/dm ² .	Deposit
30	12	Dull white; Chromium
30	15	Dull grey; Chromium
48	15	Light grey; Chromium
60	20	Dull grey; Chromium
75	15	Dull white; Chromium
100	15	Dull grey; Chromium

Table XII shows that, in excess HCl, only chromium is deposited. It was concluded that the composition of the deposit was in a large manner determined by the acidity of the electrolysis bath. When a solution containing excess NaOH was used, the deposits were spongy crusts and non-metallic.

The addition of HCl in small quantities resulted in adherent metallic deposits.

Since the conditions seemed to favor chromium deposition over nickel deposition, Bath V was prepared, containing 245 gm. NiSO_4 , 125 gm. CrO_3 , and 7.5 gm. NiCl_2 per liter. The Cr:Ni ratio was now 2:1 instead of 3.8:1 as before. Over a range of current densities from 12-20 amp./sq.dm., the solution now yielded only nickel in good amounts, but the surface was dull though adherent. During the electrolysis, the bath temperature was maintained at 25° C. and the cathodes were of copper.

TABLE XIII

EFFECT OF CURRENT DENSITY ON BATH V

Current Density amp/dm ² .	Temp.	Deposit
12	25°	Dull grey; nickel
15	25°	Dull on front; bright on back; Nickel
20	25°	Dull grey, adherent; Nickel-slight chromium

In order to effect chromium deposition from this bath, which already yielded good nickel deposits, Bath VI was used, containing 25% additional CrO_3 . The CrO_3 content was now 156 gm./l. but the NiSO_4 and

NiCl_2 contents remained as in Bath V; 245 and 7.5 gm./l. respectively. The metal ratio in the solution was now 2.5:1. More consistent results were obtained with this bath than with any previously used; that is, the composition of the deposit was not changed by a slight change in acidity.

TABLE XIV
EFFECT OF CURRENT DENSITY ON BATH VI

Current Density amp/dm ² .	Temp.	Cathode	Deposit
15	25°	Pt	Dull grey; coarse; Chromium-nickel
15	25°	Cu	Smooth white; adherent; Nickel
20	25°	Cu	Smooth white; adherent; bright on back; Chromium-nickel
25	25°	Cu	Smooth white; adherent; Chromium-nickel

It was found that higher current densities were required to deposit the alloy than with other baths. A smooth, fine-grained deposit was formed after 5-10 minutes immersion, while after running the bath for a period of two hours, the surface of the metal was streaked with grey and presented a dull appearance.

Bath VI was agitated while in operation and, unlike previous baths, a more even distribution of metal on the cathode was effected. Bath VI without agitation, gave deposits which were coarse at the edges with considerable tracing. This was remedied by agitation, while in previous solutions, agitation had little effect. The coarseness around the edges and bottom was probably due to the small bath used.

Further experiments performed under the above conditions, resulted in adherent, though not lustrous, deposits.

Composition of bath	156 gm. CrO_3 /l. 245 gm. NiSO_4 /l. 7.5 gm. NiCl_2 /l.
Current density	25 amp./sq. dm.
Temperature	32° C.
E.M.F. across cell	6.7 - 7 volts
Cathode	copper
Anode	lead
Time of deposit	120 minutes

Analysis of Deposit:

Nickel	63.6%
Chromium	36.4%

CONCLUSION

This investigation shows that an alloy of chromium and nickel can be electrodeposited from an aqueous solution.

A satisfactory electrolysis bath consisted of 156 gm. CrO_3 /l., 245 gm. H_2SO_4 /l., 7.5 gm. $NiCl_2$ /l. The optimum temperature was 25° C. and the current density used was 20 - 25 amp./sq.dm.

The resulting alloys were, in general, grey in color and adherent, but varied considerably in smoothness and lustre. The most important factors investigated, affecting the composition and character of the deposits were: concentration, current density, acidity, temperature and base metal.

(1) Concentration. Electrolysis baths containing Cr:Ni ratio of 2.5:1 and containing approximately 156 gm. CrO_3 and 245 gm. H_2SO_4 per liter, gave the best results with varying conditions of current density.

(2) Current density. At low current densities, in general, below 10 amp./sq.dm., neither chromium nor nickel are deposited from this bath. From 10-20 amp./sq.dm., the deposit contained more nickel, and

above 20 amp./sq.dm. the quantity of chromium in the deposit increases.

(3) Acidity. The deposits contained no nickel from solutions to which additional acid was added. Solutions to which excess NaOH was added resulted in the deposition of neither metal. The best results were obtained, when the solution was prepared by dissolving and mixing the salts.

(4) Temperature. Increasing the temperature has but little effect on the composition of the deposits.

(5) Base metal. In all cases, iron gave burnt, rough deposits, and often hindered chromium deposition. Platinum favored deposition of both metals but gave rough deposits with large, loose crystals. Copper was found to give better deposits under identical conditions than the other metals studied.

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