THE ELECTRO-DEPOSITION OF NICKEL

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THE ELECTRODEPOSITION OF NICKEL

by

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The purpose of this investigation is to determine what effect the compounds commonly associated with nickel sulfate in a nickel plating solution have upon the quality of the plated surface. The temperature and pH were varied so that their effect could be noted and current efficiency studies were made. As a follow-up of this work a bright nickel solution was prepared and the bright range was ascertained using the temperature and pH as variables.

Several research workers have studied similar aspects of this same problem. M. A. Brochet (1) states that a solution of nickel salt alone cannot be used for electrolysis: in the case of the chloride, nickel hydroxide forms on the cathode. With nickel sulfate the solution becomes acid upon electrolysis, as the nickel anode being passive, sulfuric acid is formed. Addition of chlorides suppresses this anodic passivity but forms anions of nickel tetrachloride with the tendency to produce nickel peroxide. A better method to suppress the acidity is to add slightly dissociable salts, such as sodium citrate. The most convenient to use is boric acid, which serves to compensate the action of the hydroxide.

Joseph Haas (2) conducted a series of experiments to determine the effect of adding various salts and acids to a bath containing 90 grams per liter of nickel sulfate. He found that the electrolysis of the nickel sulfate solution alone yielded no electrodeposited metallic nickel, but produced instead a gelatinous precipitate of nickel hydroxide. The addition of ammonium chloride and sodium citrate to the nickel sulfate solution gave

good deposits of nickel, while sodium chloride and magnesium sulfate as addition agents prohibited the deposition of nickel. The inorganic acids nitric, hydrochloric and sulfuric caused excessive hydrogen evolution and produced brittle deposits of nickel. Phosphoric acid gave a precipitate of nickel phosphate, while boric acid gave satisfactory results both in color and character of the deposits.

As the effect of zinc as an addition agent was studied it is relevant to note the results of an investigation carried out by Vozdvizhenskii and Makolkin (3). They found that satisfactory deposits of nickel can be produced up to a concentration of zinc of 0.45% of the nickel present, at various bath temperatures and at a current density of 0.05 to 1.0 amperes per square decimeter. At a higher zinc concentration, between 0.45 and 0.65% streaky deposits can be avoided by increasing the temperature to 40°, but at concentrations of zinc above 0.65% streaky deposits are inevitable. The pH around the cathode increases with increasing concentration of zinc salts, reaching such a high value that a colloidal basic precipitate of nickel salts occurs. The positively charged particles of this colloid are transported to the cathode surface and deposited as a dark layer, this condition is facilitated by the stream of evolved hydrogen at the cathode.

M. Waite (4) found that the equilibrium pH of nickel chloride decreased with increased concentration of nickel chloride. Harder deposits were obtained with increased concentration of nickel chloride and the effects are reversed as the temperature is raised.

M. R. Thompson's (5) results indicate that in general good nickel deposits are secured when the cathode current efficiency is high. He also found that at a low pH better deposits are obtained at a high rather than at a low current density. Also, deposits from a solution having a low pH are apt to be brighter, harder, finer grained and more brittle.than those from a solution of high pH. With any pH above 6.0 the deposits were found to be dark colored and cracking and curling was apt to occur.

Experimental Procedure: Before the actual results are presented the method observed in preparing the surface for electrodeposition will be given. The steel plates were first polished using a saponifiable emery compound, then they were cleaned electrolytically in a proprietary cleaner containing 6 ounces per gallon of Matawan #2. The plates were then rinsed in running water. They were then copper plated in a copper cyanide solution having the following composition: copper cyanide, 3 ounces per gallon; sodium cyanide, 4.5 ounces per gallon and sodium carbonate, 2.0 ounces per gallon. After being copper plated they were rinsed, dried and buffed using tripoli for the buffing compound. Then the panels were colored using Acme white finish.

The next step was to clean the copper plates electrolytically in a similar cleaner to the one used for the steel, the difference being that the concentration of Matawan #2 was 2 ounces per gallon. The panels were then rinsed in water, dilute sulfuric acid and then dried by first immersing the plates for

one minute in boiling water and allowing the moisture to evaporate in the air. The plates were next weighed to 0.0001 grams using analytical balances. Following that they were recleaned and plated in the nickel solution, dried and reweighed.

A stock solution of nickel sulfate was prepared containing a concentration of 32 ounces per gallon of the salt. Panels were run from the stock solution alone and then from solutions containing the stock solution plus the addition agent. In other words, pairs of compounds were used in all solutions used for electrodeposition except the first which contained only nickel sulfate.

In each series the pH was varied from 6.0 to 1.0, using sulfuric acid to lower the value and nickel carbonate to raise the pH. The pH values were determined electrometrically using a quinhydrone electrode. Two temperatures were used: namely, 25 and 40°.

The baths consisted of 1½ liters of solution in 2 liter museum jars. It was possible to operate four solutions at the same time by utilizing a water bath especially constructed for this purpose.

Experimental Results: The first series was prepared using a portion of the stock solution, which contained 32 ounces per gallon of nickel sulfate. To determine whether there was an advantage in using the chemically pure nickel sulfate or whether the commercial grade was suitable, duplicate series were made. The commercial nickel sulfate was purified preceding operation of the solution by raising the pH with a nickel carbonate treat-

ment. This treatment consists of heating the solution to 60° C. followed by the addition of a thin paste of nickel carbonate. The solution was then agitated mechanically for one hour and allowed to stand over night. The solution is then filtered from the excess nickel carbonate and from the metallic hydroxides that have precipitated. Accompanying the actual precipitation of impurities there is some adsorption of organic and inorganic contaminants on the surface of the freshly prepared nickel hydroxide. The pH obtained by this method was determined to be between 6.3 and 6.4. This preliminary purification of commercial nickel sulfate produced a solution which electrodeposited nickel identical in appearance to plates secured from a solution prepared from chemically pure nickel sulfate. Consequently commercial nickel sulfate was utilized throughout the project being purified first with nickel carbonate.

It is observed in Table 1 that a pH of 6.2 produces deposits of lower current efficiency than a solution having a pH of 5.7. This is due to the increased alkalinity of the cathode layer which facilitates precipitation of basic nickel compounds having a lower weight than metallic nickel. As the pH is decreased the current efficiency decreases also. This is due to the fact that the h drogen overvoltage on nickel decreases with increasing acidity of the solution.

Electrolysis of the nickel sulfate solution at a pH of 2.0 results in a slight increase in current efficiency over the efficiencies of the solution at higher pH values, namely, 3.0 to 4.0. At this pH either the hydrogen overvoltage on nickel

increases somewhat or the nickel overvoltage on nickel decreases. No investigation was made of the true reason for this phenomenon in this study.

It is also observed that an increase in current density with the temperature remaining constant, namely, 25°, results in a dimunition of the current efficiency. This is a reasonable effect in consideration of the fact that the conductivity of nickel sulfate solution alone is low. Any factor that would increase the conductivity of the solution would be expected to raise the current efficiency. Thus, elevating the temperature of the solution to 40° and in this manner increasing the conductivity will increase both the current efficiency and the quality of the deposit.

Fig. 2 shows the results obtained in this series. It is observed that the deposits are uniformly poor until a pH of 2.0 is attained. At that point metallic nickel of good color and quality is deposited over the entire surface of the test panel. It is also noticed that the plates at a low current density are better in appearance than those at the higher current density. Above a pH of 2.0 at room temperature and a current density of 20 amperes per square foot, the plates are very black.

The fact that the area of metallic nickel deposits first in the center of the plate emphasizes the low conductivity of the single salt solution. Since the current distribution is least in the center of the plate the conditions at that particular area on the test panel tends to favor precipitation of the metal.

A reduction in pH improves the quality of the plate by

improving the conductivity of the solution.

The polarization required for the deposition of nickel decreases with rise of temperature but the hydrogen overvoltage behaves in the same way. Therefore, whatever the current density or the temperature a low pH will result in an appreciable evolution of hydrogen and the current efficiency will be low. However, the increased allowable rate of deposition and improved quality of the deposit greatly discount the small loss in current efficiency.

Raising the temperature to 46° increases the whiteness of the deposits and completely eliminates all burning the deposit at the high current density areas. At a pH of 5.5 the deposit botained is cracked as well as being streaked with vertical black lines. At a pH of 5.0 the dark lines have appreciably diminished, and at a pH of 2.6 they are l cated at the edge of the test panel. Below a pH of 2.6 the deposits have good ph sical characteristics and possess more luster than deposits from a solution having a higher pH.

Table I

Series A

$NiSO_4 \cdot 7H_2O$ 32 oz./gal.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
1.	10	25	20	6.2	.2746	75
2.	10	25	20	5.7	.3446	90
3.	10	25	20	3.8	.2889	79
4.	10	25	20	3.1	.2875	78
5.	10	25	20	2.5	.2810	77
6.	10	25	20	2.0	.3069	84
7.	10	25	20	1.3	.0801	22
8.	20	25	20	6.3	.3638	49
9.	20	25	20	5.5	.3113	46
10.	20	25	20	4.4	.4030	55
11.	20	25	20	3.7	.4471	61
12.	20	25	20	2.0	.4744	65
13.	20	25	20	1.5	.2886	39
14.	20	46	20	5.5	.6690	92
15.	20	46	20	5.0	.6862	94
16.	20	46	20	2.6	.5986	82
17.	20	46	20	2.0	.6132	84
18.	20	46	20	1.5	.5110	70

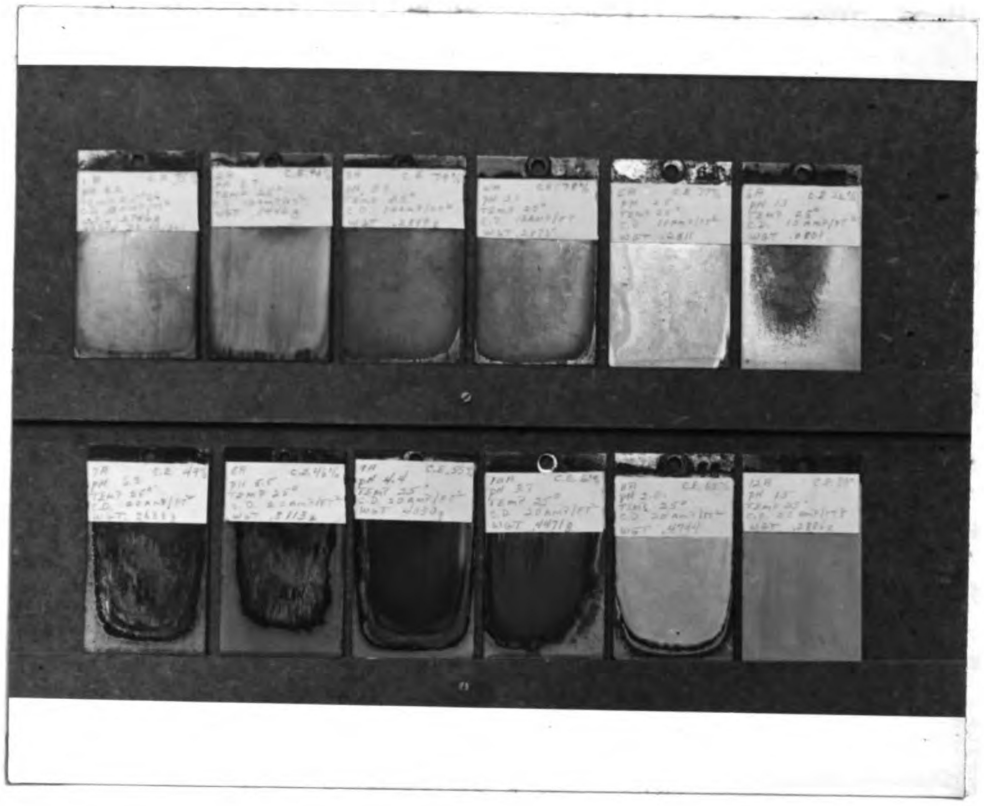

FIG. 2

In Series H the effect of boric acid additions upon the quality of nickel deposited from the sulfate solution is determinted. One of the primary observations that was made in the comparison of Table 2 with Table 1 is that the cathodic current efficiencies are greater in this series.

In the first series in the increase in temperature from 25° to 46° resulted in a marked difference in the appearance and current efficiency of the deposit obtained. However, in the present series these differences were not noted.

Boric acid has long been used for a buffer in nickel plating solutions. In this respect it acts both upon the bulk of the solution and also in the electrode-electrolyte interfacial surfaces to restrict changes in pH due to electrolysis of the solution. Boric acts in another manner in addition to its buffer action because below a pH of 4.9 it exhibits no buffer action. However, acid nickel solutions of the sulfate type about which this investigation is concerned produce excellent matte deposits at pH values ranging from 1.0 to 5.5. The presence of boric acid in the nickel sulfate solution permits a higher current density without burning or precipitation of basic nickel salts on the cathode.than can be obtained under the same conditions without it.

Fig. 3 shows that all the plates secured in this series were good matte deposits.

Table II

Series H

$NiSO_4.7H_2O$ 32 oz./gal.

H_3BO_3 4 oz./gal.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
1.	10	25	20	5.6	.3504	96
2.	10	25	20	5.0	.3472	95
3.	10	25	20	4.3	.3491	95
4.	10	25	20	3.5	.3395	93
5.	10	25	20	2.9	.3358	92
6.	10	25	20	2.5	.3285	90
7.	10	25	20	2.1	.2920	80
8.	10	25	20	1.8	.2154	89
9.	10	25	20	1.0	.0219	6
10.	20	25	20	5.5	.6059	83
11.	20	25	20	4.7	.7300	100
12.	20	25	20	4.0	.7081	97
13.	20	25	20	3.5	.6935	95
14.	20	25	20	2.5	.8790	93
15.	20	25	20	2.0	.6220	85
16.	20	25	20	1.8	.6165	84
17.	20	25	20	1.0	.0999	13

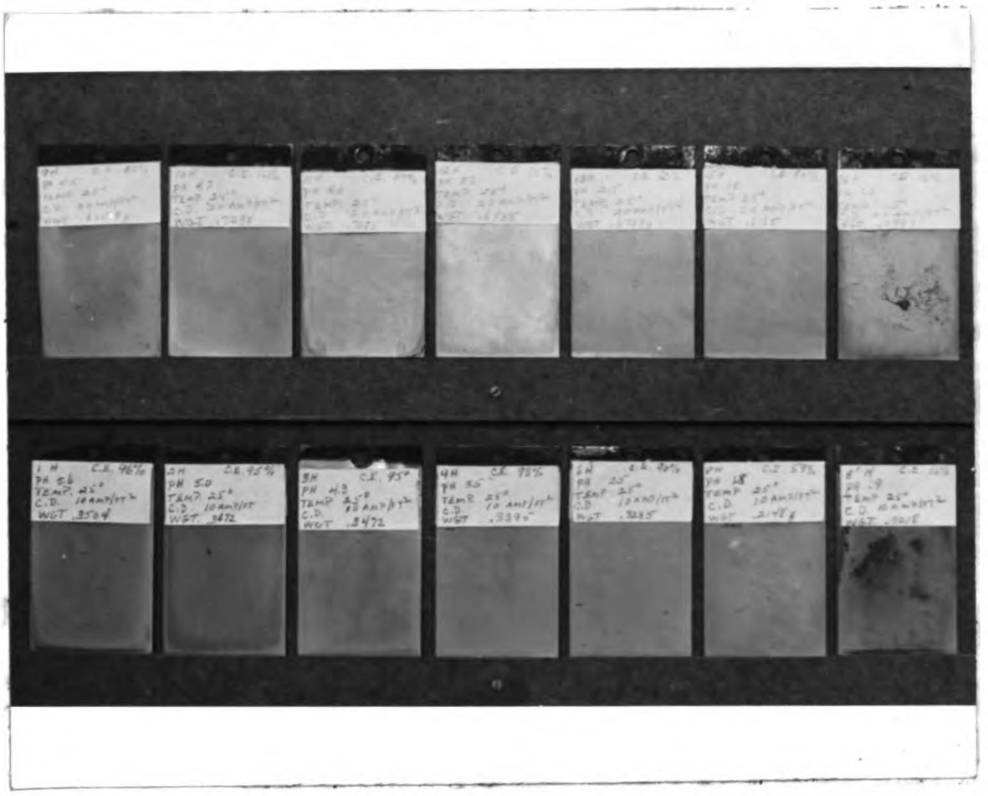

FIG. 3

Table II - Continued

Series H - cont'd.

$NiSO_4 \cdot 7H_2O$ 32 oz./gal.

H_3BO_3 4 oz./gal.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
18.	20	46	20	5.2	.7300	100
19.	20	46	20	4.5	.6555	90
20.	20	46	20	4.2	.7300	100
21.	20	46	20	3.6	.7115	98
22.	20	46	20	2.0	.6220	85
23.	20	46	20	1.1	.2285	31

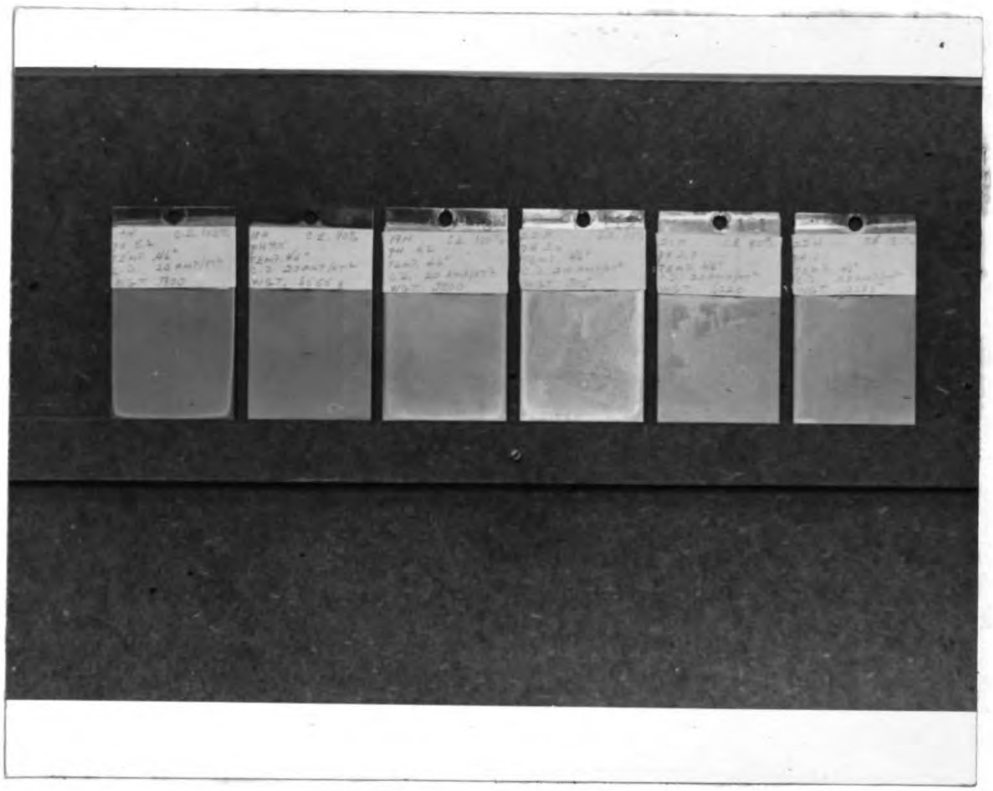

FIG. 3A

The effect upon the quality of the plate caused by the addition of nickel chloride to the nickel sulfate solution is illustrated in Fig. 4. It is noticed that the plates are very similar in appearance to the ones obtained from the nickel sulfate solution containing no addition agents.

The cathode current efficiency values are higher in this series than they were in Table I. The addition of nickel chloride to the nickel plating solution is made to provide for adequate anode solution. It is the chloride ion which is active in this respect. The chloride ion has been added as sodium, potassium and ammonium chloride and as hydrochloric acid. It is added as the nickel salt for two reasons in the first place using nickel chloride no foreign cations are added and secondly, it tends to replenish the nickel ion concentration. In addition to these reasons and perhaps or more paramount importance is the fact that a nickel sulfate solution electrolyzed with no halogen ions present becomes acid. This is due to the production of sulfuric acid at the anode and the volution of oxygen, caused by the passivity of the anode. The chloride overcomes the passive condition of the anode by acting as an anodic depolarizer. The fact that nickel chloride is highly ionized aids the conductivity of the nickel sulfate solution.

Nickel anodes are believed to be passive in a nickel sulfate bath due to the formation of a film of oxygen or an oxide which has a low oxygen overvoltage.

In a recent publication by W. A. Wesley and J. W. Carey (7) on the electrodeposition of nickel from nickel

chloride solutions they find that the deposit from a bath of this type (nickel chloride and boric acid) is finer grained, harder, stronger and somewhat less ductile than deposits from the ordinary nickel sulfate plating solution. The advantages claimed for this solution are: (1) low tank voltage; (2) ease of buffing; (3) greater smoothness of thick deposits; (4) ease of control; (5) freedom from pitting; (6) high cathode efficiency; (7) the solution has less tendency to overheat due to the passage of large currents.

The disadvantages are: (1) greater corrosiveness of the solution; (2) loss of ductility; (3) the cost is slightly higher.

Table III

Series D

$NiSO_4 \cdot 7H_2O$ 32 oz./gal.

$NiCl_2$ 4 oz./gal.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
1.	10	25	20	6.3	.2597	71
2.	10	25	20	5.1	.2671	73
3.	10	25	20	4.9	.2957	81
4.	10	25	20	4.2	.2739	75
5.	10	25	20	3.5	.2991	81
6.	10	25	20	2.9	.3000	82
7.	10	25	20	2.0	.2906	79
8.	10	25	20	1.6	.2143	58
9.	10	25	20	1.1	.1349	36
10.	20	25	20	6.0	.4138	57
11.	20	25	20	5.5	.4166	58
12.	20	25	20	5.2	.3697	50
13.	20	25	20	4.1	.4081	56
14.	20	25	20	3.6	.2842	39
15.	20	25	20	3.3	.4185	57
16.	20	25	20	2.2	.4515	62
17.	20	25	20	1.6	.5407	75

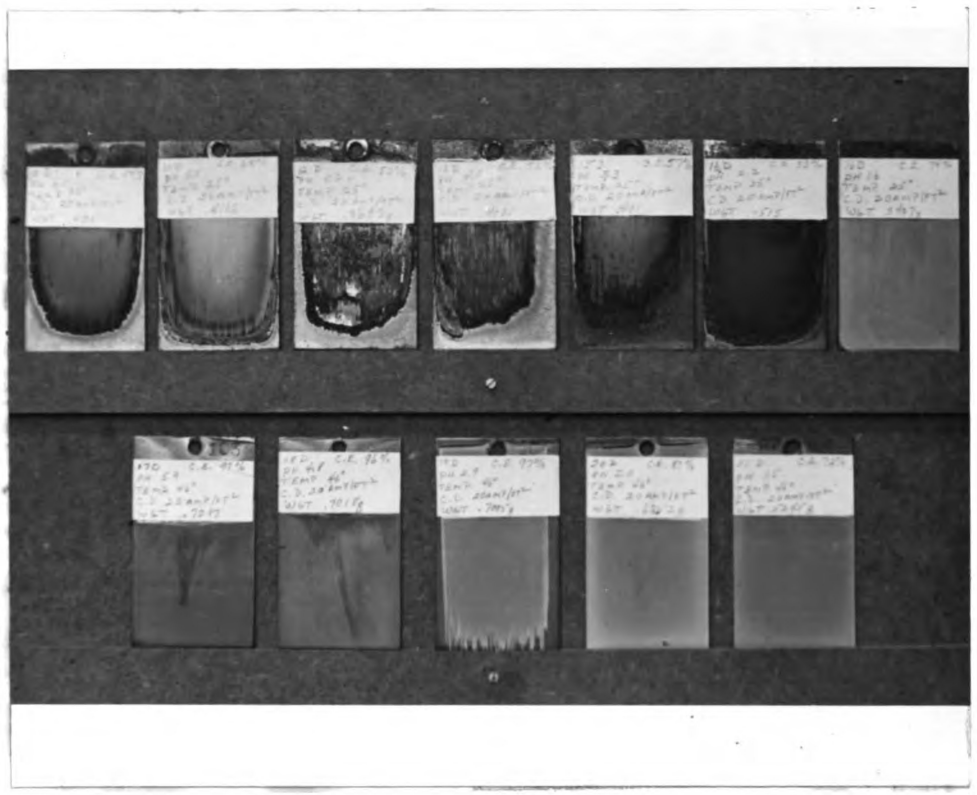

FIG. 4

Table III - Continued

Series D - cont'd.

$NiSO_4.7H_2O$ 32 oz./gal.

$NiCl_2$ 4 oz./gal.

Plate Number	Current Density Amps/sq ft	Degrees C. Temperature	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
18.	20	46	20	5.9	.7097	97
19.	20	46	20	4.8	.7018	96
20.	20	46	20	2.9	.7095	97
21.	20	46	20	2.0	.6352	87
22.	20	46	20	1.5	5245	72

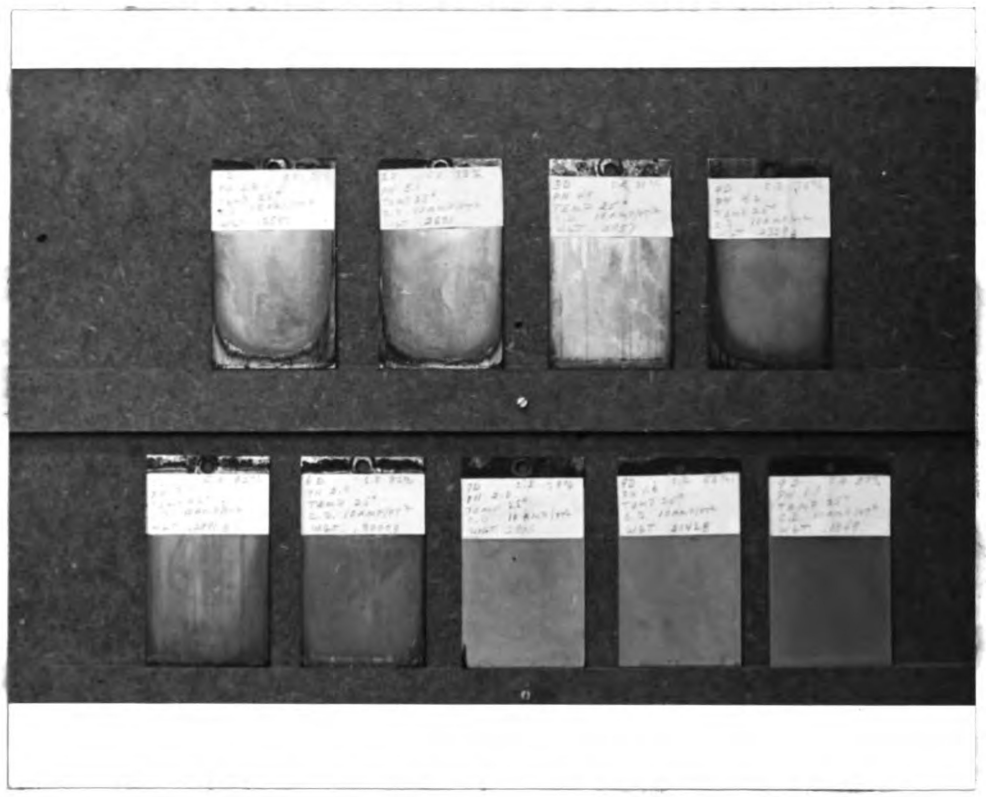

FIG. 4A

Fig. 5 shows the results obtained by adding sodium benzene disulfonate to the nickel sulfate solution. It is observed that three of the plates at the lower temperatures have bright areas. These plates occur at the pH values of 4.7, 2.4 and 1.5 with the plate from the solution at a pH of 1.5 bright over nearly the whole surface. It is also noted that at 46° there is no bright area at all. In Table 4 we notice that the current efficiency is not materially affected by this addition. The important fact is that the quality of the plated surface is markedly improved.

Salts of this type, polysulfonates, have been advocated by many investigators as being capable of producing lustrous plates from nickel sulfate solutions containing nickel sulfate, nickel chloride and boric acid. The bright plates occur at the lower pH values due to the fact that the polysulfonates tend to decompose at high pH values. Even at a pH of 4.0 the cathode layer is more alkaline than the remainder of the solution. Part of the brightening action of sodium benzene disulfonate may be due to the presence of the sodium ion, but the same brightening action has been observed when nickel benzene disulfonate or benzene disulfonic acid has been used in place of the sodium salt.

Table VIII

Series M

$NiSO_4 \cdot 7H_2O$ 32 oz./gal.

Zn 100 mg./l.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
1.	20	25	20	6.2	.3167	43
2.	20	25	20	4.9	.4685	64
3.	20	25	20	4.3	.2821	38
4.	20	25	20	3.9	.2210	30
5.	20	25	20	2.4	.4255	58
6.	20	25	20	1.5	.4538	63
7.	20	46	20	6.3	.7163	98
8.	20	46	20	3.8	.6275	85
9.	20	46	20	3.3	.6779	93
10.	20	46	20	2.6	.6299	87

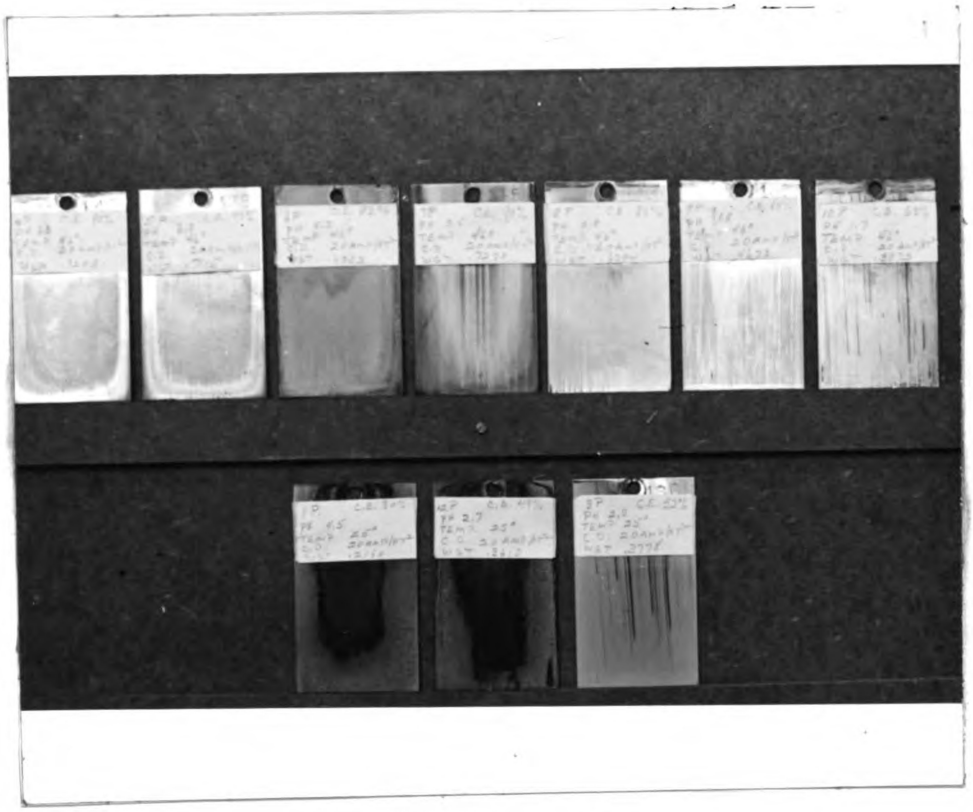

FIG. 9

Series J, M. R and P are grouped together because they deal with the effect of adding zinc in varying concentrations to the nickel sulfate solution. Series J contained 50 milligrams per liter, Series M had 100 milligrams per liter, Series R 200 milligrams per liter and Series P 500 milligrams per liter of zinc.

Referring to the tables, it is noted that the addition of zinc up to a concentration of 200 milligrams per liter tends to slightly increase the current efficiency at 25°. At a concentration of 500 milligrams per liter and an operating temperature of 25° the current efficiency drops off somewhat. However, at 46° the cathodic current efficiency is nearly the same irrespective of the zinc concentration.

Figures 6, 7, 8 and 9 show that increasing the zinc concentration improves the quality of the plates up to a concentration of 200 milligrams per liter of zinc at 25° and above that value it has the opposite effect. At 46° 500 milligrams per liter of zinc gives the best results in quality and current efficiency. at 25° and at low zinc concentrations there is a darkening of the deposit that is diminished as these two variables are increased. The zinc was added as the sulfate in all cases. The purpose for adding zinc to a nickel bath is for the production of lustrous plates. An aromatic sulfonated compound is added in conjunction with zinc when bright plates are desired. Zinc is deposited with nickel but in a low percentage.

Table VII

Series R

$NiSO_4 \cdot 7H_2O$ 32 oz./gal.

Zn 200 mg./l.

Plate Number	Current Density Amps/sq ft	Temperature Degrees C.	Time in Minutes	pH	Weight of Deposit in grams	% Current Efficiency
1.	20	25	20	6.2	.5556	76
2.	20	25	20	4.4	.3544	49
3.	20	25	20	3.6	.4600	63
4.	20	25	20	2.9	.3869	53
5.	20	25	20	1.5	.2419	33
6.	20	46	20	5.8	.7300	100
7.	20	46	20	5.0	.6665	91
8.	20	46	20	4.3	.6875	94
9.	20	46	20	3.5	.6839	94
10.	20	46	20	2.8	.7000	96
11.	20	46	20	2.0	.7003	96
12.	20	46	20	1.6	.5058	70

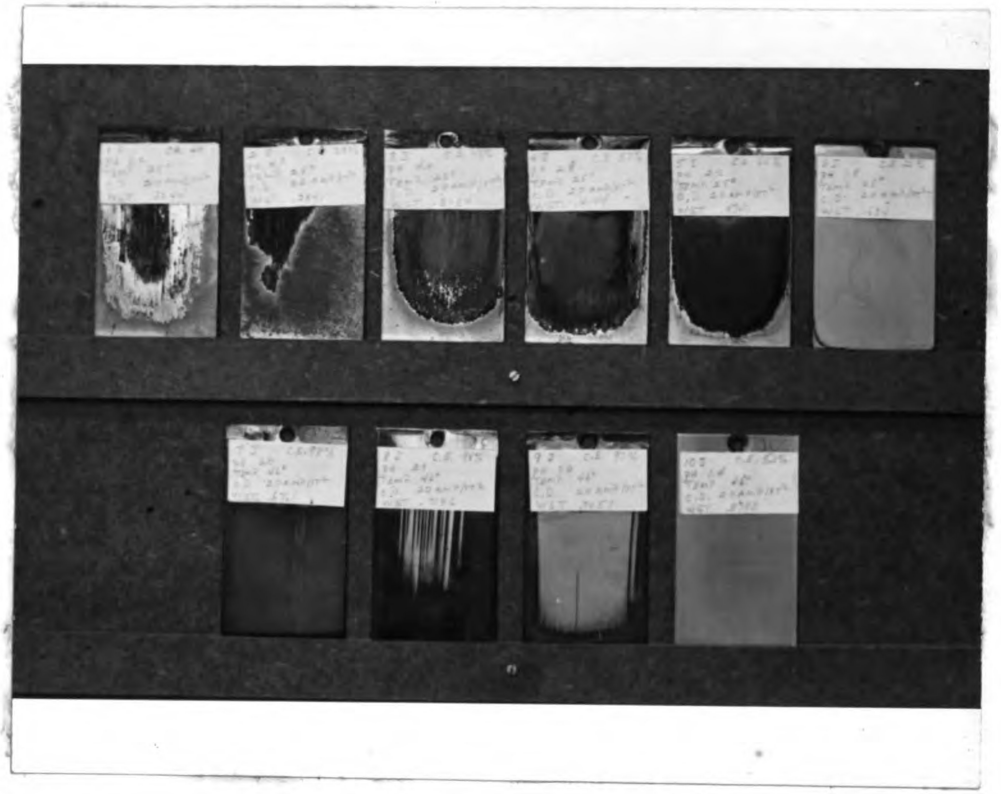

FIG. 6

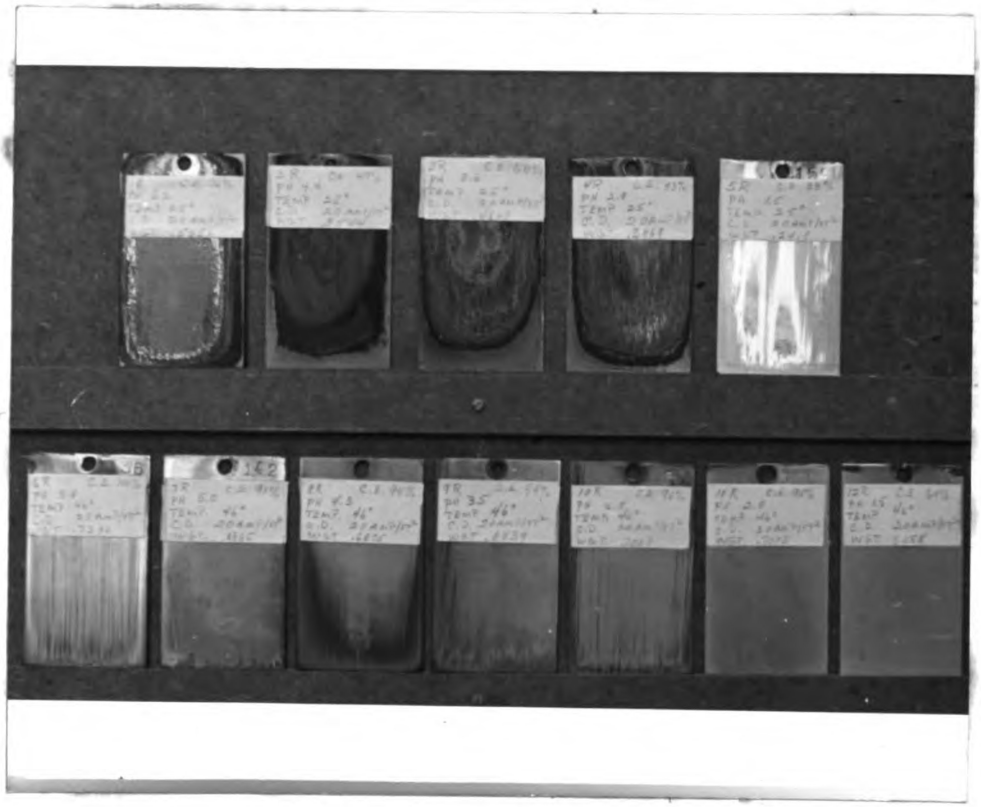

FIG. 8

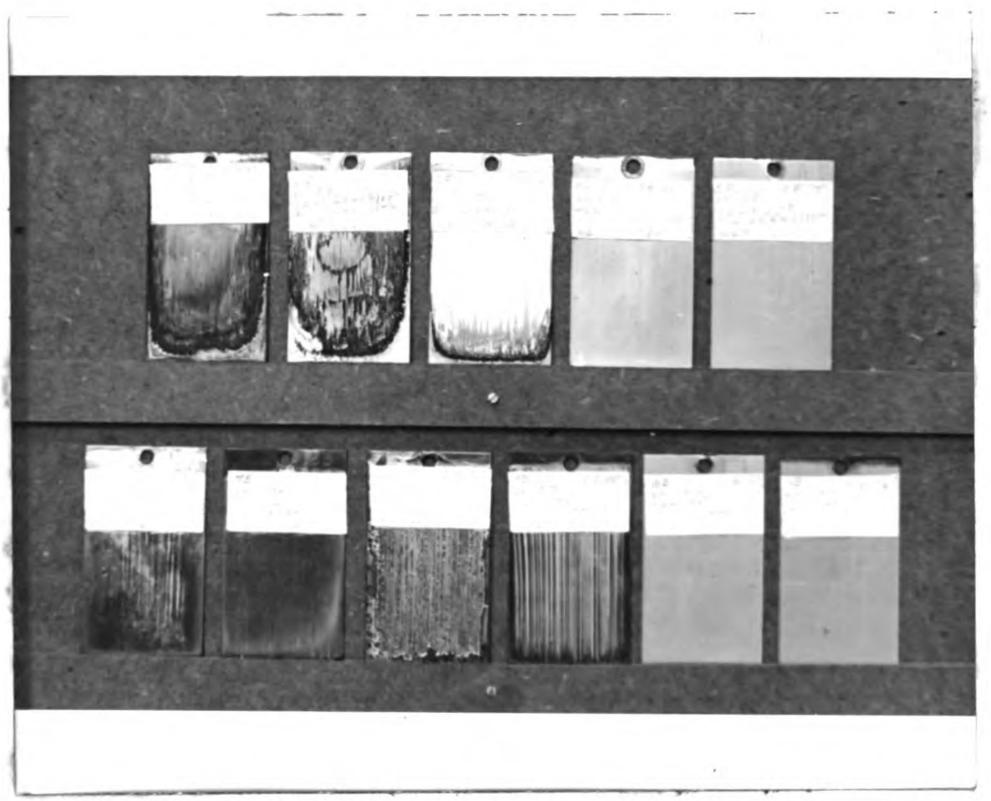

FIG. 10

A resume of the results obtained discloses several interesting points. In the first place, deposits of nickel can be obtained from a bath containing only nickel sulfate in a concentration of 32 ounces per gallon. At the higher p H values there is a preferential deposition of basic nickel salts on the cathode. However, at approximately a pH of 2.0 the quality and appearance of the plate is good. If the bath is operated at a pH above 2.5 the tendency is for the solution to become more acid. Operation of the bath below a pH of 2.5 causes only a slight change in pH. It is apparent that the relative cathode and anode efficiencies are nearly identical below a pH of 2.5, thereby maintaining a constant pH in the solution.

An increase in temperature caused the cathode current efficiency to increase by diminishing the tendency for the deposition of basic salts. An increase in the current density at 25^{o} caused the cathode current efficiency to decrease because the poor conductivity of the solution promoted a greater deposition of basic salts on the cathode.

The addition of nickel chloride tended to darken the deposit. However, the provision for efficient anode corrosion maintained the pH at a more constant value upon electrolysis of the solution. Variations in the temperature, pH and current density produced essentially the same results that were obtained in the nickel sulfate solution with no addition agents. It was again noted that at a pH of 2.5 to 2.0 the deposit improves greatly due to total elimination of all traces of basic salt precipitation on the cathode. An increased temperature again

improved the current efficiency and appearance of the plated specimens.

The addition of boric acid very positively improved the quality of the plate and the current efficiency of the solution under all conditions investigated. The presence of the boric acid enabled maintenance of pH values above 4.9 by effectively buffering the solution. Below a pH of 4.9 its buffering value is very limited. In all cases the deposit was white in color and matte in character. In this series the improvement in current efficiency upon increasing the temperature was not appreciable.

The addition of sodium benzene disulfonate produced bright areas on the test panels at 25° and pH values of 4.7, 2.4 and 1.5. At a pH of 1.5 the bright area covered nearly the whole plate. Increasing the temperature resulted in loss of the bright area but increased current efficiency.

The addition of formaldehyde produced poor plates when the pH of the solution was in excess of 2.5. An increase in operating temperature did not improve the quality of the deposits. At 25° and a pH of 2.5 a bright area occurred that was not present in any of the other panels. At 46° and above a pH of 2.2 the deposits obtained were ridged vertically. A peculiar point concerning this addition agent was the fact that at room temperature the current efficiency increased as the pH decreased, indicating quite clearly the fact that formaldehyde acts as a cathodic depolarizer and is most effective in this respect at a low pH.

Concentrations of zinc in the nickel sulfate solutions up to 200 milligrams per liter improves the quality of the plated

surface and the current efficiency when the operating temperature, is 25°. A concentration of 500 milligrams per liter of zinc and a solution temperature of 25° had the opposite effect. At 46° the current efficiency is approximately the same at all concentrations of zinc, but the quality of deposits from the solution having a concentration of 500 milligrams per liter of zinc were superior. An increase in temperature improved all the deposits somewhat.

With regard to the results that were obtained at low pH values, Dr. A. Kenneth Graham (8) published an article indicating that a Watts type bath operated at a pH range of 1.0 to 2.5 rather than the customary range of 5.6 to 6.0, can be operated at current densities well in excess of 100 amperes per square foot and still produce satisfactory results. The current efficiency drops at the low pH values advocated but the increase in allowable current density favors more rapid deposition and the wider plating range produced deposited plate less subject to cracking and roughness at the edges.

The advantages that Graham claims are: (1) increased plating range, which embodies decreased time and increased current density; (2) better anode corrosion; (3) no turbidity. The disadvantages are: (1) lower cathode efficiency; (2) too high anode corrosion in some instances; (3) the high temperatures used restrict some types of tank linings; (4) for bright nickel plating the low pH bath gives the best results at a low temperature; (5) low pH solutions are not suitable for plating zinc base die castings.

S. Makaieva (9) investigated the effect of the composi-

tion of the electrolyte, current density and bath temperature upon the properties of electrolytic nickel and recorded the following data. He deposited nickel on polished copper cathodes under two different conditions, (1) current density of 0.1 amperes per square decimeter at 20°, (2) a current density of 5 amperes per square decimeter at 60°. The electrolyte was not agitated, the pH was constant at 5.3 and the luster, hardness, porosity, microstructure and crystal orientation of nickel layers 20 microns thick were determined for various current densities, temperatures and bath compositions. All the nickel deposits from chloride baths had a yellow tinge, were less lustrous, less orientated, but considerably harder and more porous than deposits obtained under the same conditions from sulfate baths. The differences in properties were more pronounced at 60°. By increasing the current density the hardness of the nickel deposit obtained from the sulfate baths decreased and the luster improved, but for nickel deposited from the chloride baths the opposite effects were obtained at 60°.

A summary of the results obtained by the author in his investigation is as follows:

1. (a) Nickel sulfate in a concentration of 32 ounces per gallon can successfully be utilized with no addition agents for the production of electrodeposits of nickel if the pH is maintained below 2.5.

   (b) An increase in current density at 25° decreases the current efficiency.

   (c) Increasing the temperature to 46° improves the

current efficiency and the quality of the deposit.

(d) Above a pH of 2.5 the solution becomes more acid upon electrolysis.

2. The addition of nickel chloride causes the anodes to corrode, helps to maintain pH values and causes a darkening of the deposit.

3. Boric acid improves the quality of the deposit, improves the current efficiency and acts as a buffer above a pH of 4.9.

4. Sodium benzene disulfonate at 25° produced deposits having bright areas at pH values of 4.7, 2.4 and 1.5.

5. The addition of zinc at 25° improved the current efficiency and plate quality up to a concentration of 200 milligrams per liter, above that opposite effects were produced. At 46° the current efficiency was approximately the same in all cases. At 46° the plate quality is improved as the zinc concentration is increased and is best at a concentration of 500 milligrams per liter.

6. The addition of formaldehyde to the nickel sulfate solution produced a lustrous plate at a pH of 2.5 and at an operating temperature of 25°. It also resulted in increasing the current efficiency at 25° as the pH decreased.

7. In general good deposits were secured from all bath compositions at pH values below 2.5 and at both 25° and 46°. The exception was the nickel sulfate solution containing boric acid as an addition agent in this series all the deposits were satifactory.

The next section of this study was a bright range investigation. In this part the current density in all tests was kept at a constant value of 25 amperes per square foot. The variables were pH, temperature and brightener concentration. The object was to determine the best operating conditions for the production of lustrous deposits from a bath having the following composition: nickel sulfate, 32 ounces per gallon; boric acid, 4 ounces per gallon; nickel chloride, 4 ounces per gallon; sodium lauryl sulfate, 67 milligrams per liter; zinc, 200 milligrams per liter; benzene disulphonic acid, 5 grams per liter.

The cathodes were 0.1 square foot steel plates which were plated in a cyanide copper solution and then color buffed. The buffed copper plates were electrocleaned in a solution containing 2 ounces per gallon of Matawan #2, rinsed in distilled water, given an acid dip in 20% sulfuric acid, rinsed again in distilled water and were then electroplated in the nickel solution.

The functions of the constituents were as follows: the nickel sulfate was present to provide the main source of nickel; the nickel chloride furnished nickel ions, improved the conductivity of the bath and provided for adequate anode corrosion; boric acid improved the quality of the deposit, increased the current efficiency and acted as a buffer between a pH of 4.9 and 6.0; sodium lauryl sulfate decreased the surface tension of the solution and in that way eliminated pitting of the deposit due to adhesion of hydrogen on the surface of the cathode during deposition; the zinc and benzene disulfonic acid were the brighteners.

The pH of the solution was lowered with sulfuric acid and was raised with nickel carbonate. To determine the pH an electrometric method was used which was composed of a quinhydrone-calomel cell used in conjunction with a Leeds and Northrop potentiometer.

The temperature range studied was between 87° and 135° F. The pH range was from 5.5 to 1.0 Figure 11 shows a graph outlining the range within which the most lustrous deposits were secured.

The bath as originally prepared had a low pH and was raised using nickel carbonate to a pH of 5.9. At this pH the deposit has a tendency to be streaked and burned in the temperature range of 75° to 90° F. and in addition are pitted. Between 95° and 120° F. the deposits are not streaked or burned and the pitting is approximately eliminated but the plates are very gray in color. Despite the grayness of the deposit the appearance is more lustrous than a matte nickel deposits.

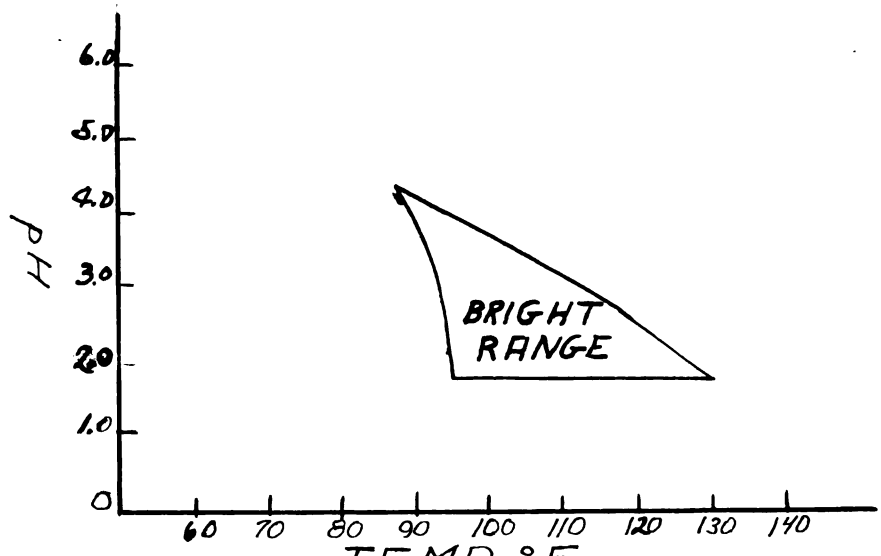

FIG. 11

The effect of lowering the pH to 5.0 was to improve the brightness of the plates in the low temperature range, 75° to 100°, but the panels were still burned on the edges until a temperature of 90° was attained. Above 90° the plates were all pitted and became increasingly more gray as the temperature was increased.

The pH was then decreased to 4.0 and the result was to further improve the brightness of the low temperature deposits, which again became progressively grayer as the temperature was raised. Even the plates secured below a temperature of 110° had a slight surface cloudiness that eliminated any from the category of bright nickel deposits. The degree of pitting was appreciably reduced and burning was noticed only on the plate at 75° . The burning in this instance was not the black deposit hitherto secured but had instead a matte appearance.

At a pH of 3.6 the deposits were all good and below 110° were quite lustrous except in the center of the panel where a cloudiness was still observed. The pitting was entirely eliminated.

Again reducing the pH this time to 3.1 produced plates in the temperature range 85° to 92° upon which only an extremely faint cloud could be observed. The depth of grayness still increases with increasing temperature. Even at a temperature of 122° they were more lustrous than any plates secured down to a pH of 4.0.

At a pH of 2.5 the grayness was appreciably diminished throughout the temperature range. The deposits secured between

95° and 115° were the most lustrous so far obtained.

When the pH was reduced to 1.9 it was impossible to perceive any trace of cloudiness on the surface except above temperatures of 110°. Even deposits above 110° were only slightly cloudy. However, the extreme edges were matte in appearance until a temperature of 110° was reached. A reduction in current density from 25 to 20 amperes per square foot eliminated this condition without adversely affecting the brightness.

At a pH of 1.5 practically the same results were obtained as were secured with a pH of 1.9. The differences between the results secured in this trial and at a pH of 1.9 were that the bright deposits could be secured at 132° and the matte condition on the edges was more pronounced at the low temperatures.

The effect of increasing the zinc concentration to 300 milligrams per liter and the benzene disulfonic acid to 10 grams per liter aided slightly so a new bath was prepared using the increased brightener concentrations and the entire series was repeated. The results obtained were essentially identical to the results secured in the first series.

The cloudiness mentioned was believed to be due to the presence of copper in the solution. It was proven that copper was present by immersing a nickel plated cathode in the solution for ten hours. At the end of that time observation of the electrode disclosed the fact that a visible amount of copper had deposited on the nickel by immersion. The copper present was largely removed by operation of the bath at a pH of 1.5 and utilizing a current density of 0.5 amperes per square foot for 15

to 20 hours. Plates secured after this treatment were more lustrous than those obtained while copper was present. The surface cloud was eliminated approximately 95%. However, when the pH was raised the cloudiness of the deposit reappeared. The source of copper was definitely determined to be in the Bakers C. P. nickel carbonate used to raise the pH.

A summary of the results obtained in this study is as follows:

(1) The bright range for the solution studied appears to be between 100°-130° F., the current density is 25 amperes per square foot and the pH range is 1.5 to 2.5.

(2) The presence of copper is a definite contaminant and causes the deposits to be milky.

This problem of bright nickel has held the attention of investigators for many years. Colloids were first used as brighteners. Joseph Underwood (10) states that glues, gums, etc., act as brighteners in nickel plating solutions, but they are difficult to control and cause trouble unless the amounts used are small. A slight excess causes peeling and cracking. He suggests that cadmium acts as brighteners and give less trouble. The use of cadmium as the chloride produces the best results.

Marcel Ballay (11) in an investigation of the production of bright nickel deposits by the use of colloids records the following material. Upon electrolysis of a nickel sulfate solution containing small amounts of chloride and borate with a cathode over the surface of which the current density varies

considerably, bright nickel deposits are secured in certain areas, where the pH is just below that favoring precipitation of nickel hydroxide or basic salt in the immediate proximity of the cathode. The addition of some organic colloids, e. g., starch, dextrin, gum arabic, agar-agar, gelatin (2.5 milligrams per liter suffices with a pH of 6.5, but 0.4 grams per liter is necessary with a pH of 8.0) egg albumin and casein also gives bright deposits which are somewhat more uniform and obtainable with a greater range of current density than those obtained with inorganic additions.

It is generally known that bright deposits obtained by the use of gelatin, casein, various gums, etc., are too brittle and the operating conditions are too critical for commercial use.

Max Schlotter (12) states that bright deposits of nickel are obtained from solutions containing alkali or alkaline earch halides, eg., sodium chloride, potassium chloride, magnesium chloride, magnesium bromide, sodium iodide and aromatic sulfonic acids or their salts. The total amount of halogen and other inorganic acid radicals present should be more than equivalent to the sulfonic acid radical and the pH should be from 3.5 to 5.3, though more acid solutions may be used with higher current densities. Nickel may be introduced into the bath as nickel sulfate, nickel carbonate and/or nickel hydroxide. In examples the aromatic sulfonic acid compounds used are sodium toluenedisulfonate, sodium trisulfonate, naphthalenedisulfonic acid and sodium benzenedisulfonate.

Priston and Gardam (13) found that nickel was deposited

in a smooth, lustrous form from a bath containing an organic sulfonate in addition to a colloidal substance, e. g., gelatin and/or lysalbic acid. The monosulfonates were found to be particularly suitable. The sodium sulfonates of benzene, toluene, ethylbenzene, iso propylnaphthalene, triphenylpentane, alkyl naphthalene, tetrahydronaphthalene and pyridine are specified. They also recommend that the pH may be buffered by the addition of boric acid, acetic acid, formic acid and adipic acid or their salts.

W. Machu (14) states that colloids and substances of high molecular weight are adsorbed on the cathode during electrodeposition, forming a porous diaphragm with a "pincushion" structure. The discharge of the cations and the deposition of the metal is believed to occur in the intermicellar spaces in the diaphragm. Since the pores are small the crystal nuclei are small and their number is high and thus they give a fine-grained deposit. Growth of the nuclei is hindered by the reduced rate of diffusion of ions in the colloidal diaphragm. Uniformity of structure is attributed to restriction by the pores in the direction of growth of the metal crystals.

At the present time bright nickel solutions based upon the addition of aromatic sulfonic acid compounds or their salts and used in conjunction with a metal such as zinc are in wide use in commercial plating. They are in general quite satisfactory and have a pH range of 2.5 to 3.5, a temperature range of 120°-145° F. and a current density variable extending from 20 to 100 amperes per square foot. The most widely used

purification of these baths consists in two operations (1) of organic contaminants by filtering through activated charcoal or an appropriate clay and (2) purification of metallic impurities by raising the pH with nickel carbonate and precipitating the contaminating metals as their hydroxides. Another type of purification applicable to metallic impurities is advocated by Louis Weisberg which consists of plating out the impurities using low current densities and a low pH.

Another bright nickel solution obtains lustrous deposits by plating a cobalt-nickel alloy. The brightness of this deposit depends upon the presence of formaldehyde and a formate in the solution. Louis Weisberg (15) states that ammonium sulfate enhances the brightness of the deposit in proper amounts but an excess results in embrittlement. Formaldehyde acts as a depitter and depolarizer. The combination of sodium formate and formaldehyde increases the effectiveness of the brighteners.

Cadmium is used in another bright nickel solution to produce deposits of high luster. E. Raub and M. Wittum (16) find that the cathode potential-current density curves obtained in baths containing 144 grams of nickel sulfate and 10 grams of boric acid per liter with a cadmium content varying between 1.3 and 12.7% of the total metal content indicate decreasing throwing power with increasing cadmium content. Considerable amounts of cadmium are deposited with the nickel, which increase with the cadmium content of the bath and decrease with increasing current density. It is concluded that cadmium additions for bright nickel baths are less suitable than organic brighteners.

Regarding the cause of the production of lustrous deposits of nickel from some baths R. Springer (17) states that the principal conditions for producing bright nickel deposits are: the microcrystals of the deposits should be so orientated that one of the reflecting surfaces lies in the plane of the surface of the object and should be smaller than the shortest wave length of light incident upon the surface.

Vozdvizhenski and Suliemanova (18) believe that the luster of bright nickel is due to an increased hydrogen content in the deposit, leading to the formation of an inner strain which causes a disintegration of the metal during the process of deposition.

Another theory advanced by M. Schlotter is that bright electrolytic deposits of metals have an extremely small grain size, of the order of the wave length of light. In controlling the grain size it is found that the anions of hydrolysis products of the salts in the electrolyte is of major importance, since these anions may be deposited with the metal and thereby influence the manner of grain formation. The greater the volume of the anion the greater the rate of grain growth of the metal and the smaller the number of nuclei formed; hence the greater the grain size.

Hothersall and Gardam (19) in an investigation on the structure and properties of bright nickel deposits state that three types of deposits were investigated: (2) nickel-cobalt alloy deposited from a bath containing sodium formate and formaldehyde, (b) nickel deposited from a bath containing 5 grams

per liter of nickel naphthalenedisulfonate, (c) nickel deposited from a bath containing 30 grams per liter of isopropylnaphthalene sulfonate. Ordinary nickel deposits appear matte, they claim, because the surface consists of irregular mounds which scatter reflected light. The mounds do not have plane surfaces or crystal facets. Bright nickel deposits have a very small grain size and the surfaces are very smooth. The luster of thin deposits was highest on a smooth fine-grained surface. On coarse-grained surfaces the deposits had to be .0004" to appear fully lustrous. The bright deposits show no definite microstructure. The etched cross-section showed large numbers of lines parallel to the cathode surface. These lines are depressions caused by preferential deposition, but no explanation is advanced. These lines were not found on deposits from solutions (b) and (c) which had been annealed in vacuo at 300°. When the annealing was done at 1000° in vacuo all three bright deposits obtained a fair grain size. The stress in the deposits was determined by the bending of a thin steel strip which was plated on only one side.

Deposits from solutions (a) and (c) had a higher stress than ordinary dull nickel, but the deposit from solution (b) had practically no stress. By a bend test deposit (a) was found to be almost as ductile as ordinary nickel. Deposits (b) and (c) were brittle. X-ray examination of (a) and (c) yielded a diffuse reflection indicating a smaller grain size matte nickel deposits. Deposit (a) showed some orientation of the crystals, but (c) die not. The porosity of bright deposits was about the same as matte deposits, except when the bright deposits contained

cracks.

The above references represent a fairly complete survey of the literature on bright nickel plating and are included to indicate the study that is being done on this problem. The subject is still comparatively new and a great deal of work needs to be done not only to clarify the mechanism by which bright deposits are secured but also development of control methods and analyses. Subsequent investigations will doubtless answer many, if not all, of the questions about which we may now only theorize.

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