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The relative merits of the electrolytic deposit and the galvanic nickel deposit when used to produce enamel adherence

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THE RELATIVE MERITS OF THE ELECTROLYTIC DEPOSIT AND THE GALVANIC NICKEL DEPOSIT WHEN USED TO PRODUCE ENAMEL ADHERENCE.

BY

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THESIS

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Purpose of This Paper:

The purpose of this paper is to determin if nickel deposited electrolytically from a nickel bath at 100°F. or less gives the same adherence qualities to enameling steel that nickel deposited galvanically at 160-180°F. produces.

Theory and Discussion of Ordinary Nickel Bath:

Most enameling plants use a nickel bath in the pickling line following the acid rinse tank. This bath places a thin film of nickel on the enameling iron which is good insurance against many defects which plaque a plant from time to time. Nickel dips materially aid in the development of adherence and in controlling the conditions that contribute to copper heading and fish scale.

The following are the factors which affect the rate of nickel deposition-- strength of solution, time of immersion in the nickel bath, nickel bath temperature, the pH of the solution, acid pickle temperature and time, type of nickel salts, and enamel iron stock.

According to Zander[1] the grams of nickel deposited

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[1] J.M. Zander, "Trend of Relation Between Nickel Deposit and Adherence," Better Enameling, Dec. 1940.

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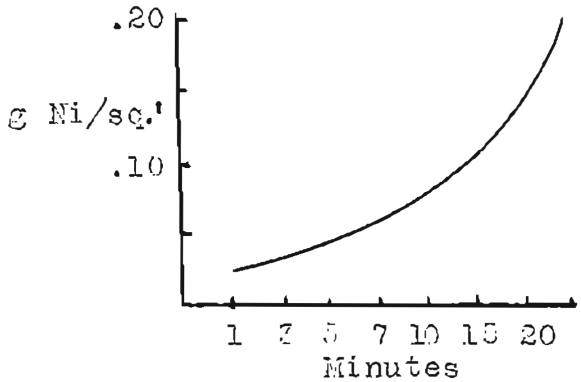
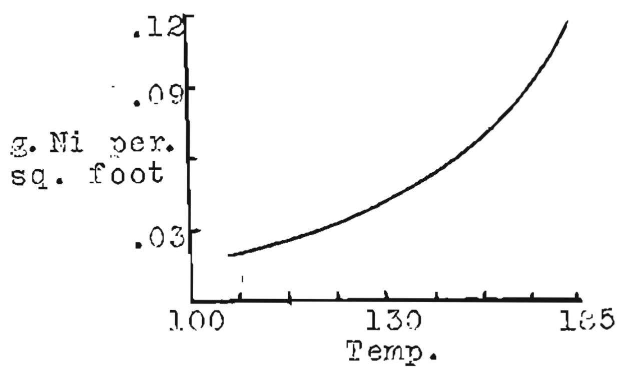
galvanically from a nickel bath will vary with temperature, time, and pH as follows:



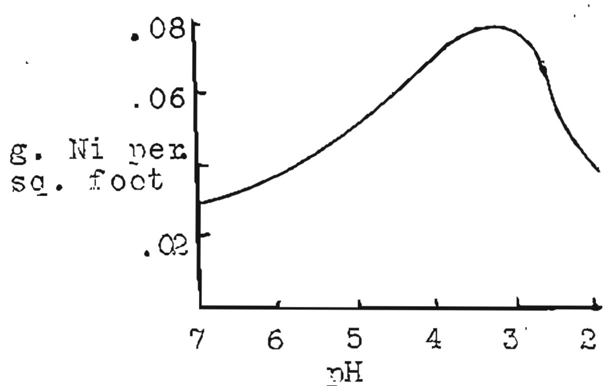
Effect of time of immersion upon the nickel deposition--

Pickle time- 10 min.
Concentration- 2 oz Ni/g.
Temp.- 150-160^{o}F.
pH- 5.8-6.2
Time- variable



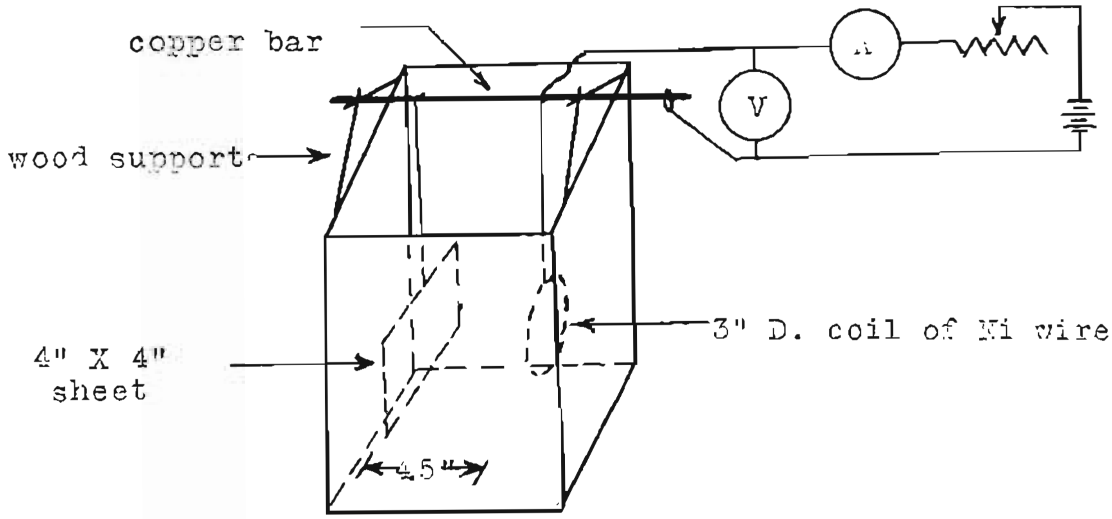
Effect of bath temperature upon nickel deposition--

Pickle time- 10 min.
Concentration- 2 oz Ni/g.
pH- 5.8-6.2
Time- 5 min.
Temp.- variable

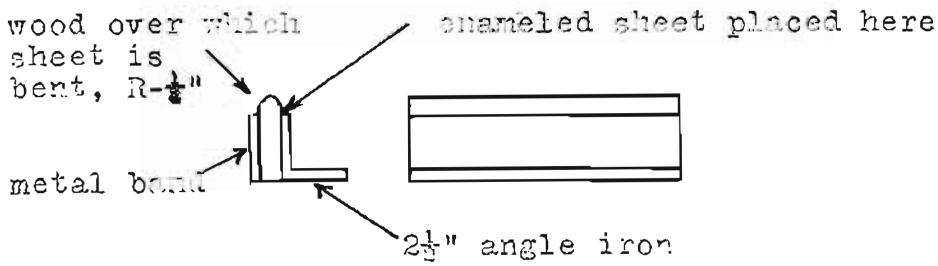


Effect of bath pH upon the nickel deposition--

Pickle time- 10 min.
Concentration- 2 oz Ni/g.
Temp.- 150-160^{o}F.
Time- 5 min.
pH- variable



Apparatus used in plating of sheets-



Bending Apparatus-

According to A.H. Haessler[1] the ideal nickel bath should have the following conditions satisfied:

2 oz. of single nickel salts per gal.
.25 oz. boric acid per gal.
pH of solution 5.6 -6.2
temperature of bath 160 to 180°F.

The above conditions along with a five minute immersion gives a nickel deposit which produces very good adherence. Comparing these conditions with those in Zander's article[2] where he gives graphs which show the weight of nickel deposited, it is found that .04 grams of nickel per square foot will be deposited. Now comparing this .04 grams of nickel per square foot with Zander's chart on good adherence, under various conditions, one finds that the .04 grams falls well within his range of good adherence. Therefore, the above conditions were used as a base for finding what effect electrolytically deposited nickel would have on the adherence of enamel.

1A.H. Haessler, "Preparation of Metal Surfaces," _A Manual of Procelain Enameling_, 1937, p. 84.
2J.M. Zander, ibid.

The Application ofElectricity to the Nickel Bath:

Since the average galvanic bath must be kept at 160 to 180°F. to plate out the amount of nickel necessary in five minutes to produce the desired adherence between the enamel and steel, it seemed feasible to produce the same results by lowering the bath temperature to 100°F. or lower and applying electricity to speed up the deposition. A bath at room temperature is an ideal set-up and it would be less costly from the standpoint of fuel necessary to produce steam to keep the bath at the customary 160 to 180°F. The working conditions will be improved by reducing the bath temperature, and the life of the tank should be prolonged.

It is understood that an electrolytically deposited nickel is a tight deposit, while the galvanic deposit is a loose deposit which can be rubbed off. A loose deposit as formed by galvanic deposition is easily taken up by the ground coat to produce adherence, while it is debatable if an electrolytic deposit will do this. The respective merits of both types of deposits were observed.

With the above in mind the following procedure was followed:

Procedure:

Tank and apparatus used-- The nickel tank was made from monel metal. The dimensions were 8" X 8" X 12" with a wooden support on each end used to support a copper bar upon which the test sheets were suspended. Four feet of nickel wire rolled into a 3" ring and suspended in the solution acted as the anode. The current and voltage was supplied by a six volt storage battery. In series with the bath and the battery was placed an ammeter and a variable resistance. A volt-meter was hooked across the nickel bath temporarily so that readings of the voltage drop across the bath could be taken from time to time. The nickel bath was kept at the desired temperature by the use of a hot plate and a bunsen burner, if the latter was necessary. The other solutions were contained in ordinary crocks and were also heated by a hot plate.

The LaMotte Roulette Comparator was used in determining of the pH. The color standard used was chlorphenol red, which has a pH range of 5.2 to 6.8.

The ground coat enamel was dried in an oven at a temperature of about 300°F. The sheets tested were fired in a small muffle furnace, automatically controlled at 850°C.

The bending tests were performed with a clamp-like device that held the enameled sheet tightly in place while the bending was done. A piece of wood was used to back up the enameled sheet. This piece of wood was shaped as shown in the drawing to assure a uniform curvature when bending the enameled sheet during the adherence test.

A drop-weight test was used to check the results of the bend test. An 1800 gram, 3.5" steel ball was dropped 18" upon the enameled sheet which was laid over a cupped shaped piece of steel that had a circular hole 3" in diameter. The ball was dropped first on one side and then on the other until bare steel was visible.

Solutions used--

cleaner- 4 oz. Oakite per gal. water.
temperature- boiling.

pickle solution- 6% H_2SO_4
1% NaCl
temperature 170°F.
time- 5 minutes.

nickel solution- 2 oz. single nickel salts./g.
.25 oz. boric acid per gal.
pH- 6.2.
temperature- and time variable.

neutralizer solution- .4% Na_2O -- equally divided between NaOH, Na_2CO_3, and $Na_2B_4O_7 \cdot 10\ H_2O$.

General Characteristics of Nickel Bath as Found by Preliminary Observation--

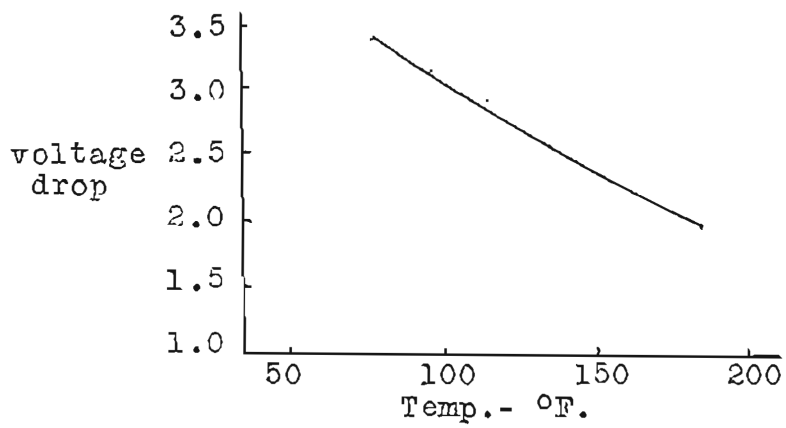
1. When no H_2SO_4 is present in the bath, the only acid being boric acid, no hydrogen is evolved at low temperatures and relatively high voltages, but if H_2SO_4 is added only in small amounts hydrogen is evolved. It was observed that the rate of hydrogen evolution increases with increase in the temperature of the nickel bath. At two volts and 180°F. no hydrogen was observed and at three and four-tenths volts and room temperature no hydrogen was evolved, but with a voltage of four volts and 180°F. hydrogen was evolved rather vigorously. The area of the cathod will determine to a limited extent whether hydrogen will be evolved or not. An extremely small cathode area makes possible hydrogen evolution.

2. When the bath is at 170°F., current and voltage through the bath is 2 amp per square foot and 2 volts respectively, and the anode-cathode distance is 4.5", the amperes and voltage do not change appreciably when the anode and cathode are brought close to one another, but as the current is raised to 4.5 amperes per square foot or more, moving of the cathode and anode together produces a marked increase in the current and voltage through the cell. This is due to the fact that the break down voltage of the solution is somewhere above

two volts and under the voltage associated with four and five-tenths amps per square foot.

3. At low voltages, 1.5 or 2 volts, when the bath is at 170°F., the area of the anode surface is no factor, but at higher voltages it is a factor.

4. Below is a graph showing the relationship between the temperature of the bath and the voltage drop through the bath:



The bath was set up as above with the temperature 170°F. Single sheets were plated for 15 and 30 minutes at 2 amperes per square foot. The amount of nickel deposited was determined.

In 15 minutes .2691 grams of nickel per square foot was deposited and in 30 minutes .7056 grams of nickel per square foot was deposited. This would indicate that as time progresses the nickel deposited per minute increases.

Using the 15 minute deposit as a standard, it was found that in one minute $\frac{.2691}{15} = .0166$ grams of nickel is plated out per square foot per minute. So in two minutes .0332 grams of nickel per square foot would be plated out. This is over the .025 grams per square foot minimum for good enamel adherence. A check was made to determine if that amount of nickel is actually plated out in that time and it was found that it is. From this it was assumed that a two minute deposit at 170°F. in the standard bath is equivalent to the 5 minute galvanic deposit at 170°F. in the standard bath. Of course it is understood that these two types of deposits, the electrolytic and galvanic, will not produce the same degree of adherence to enamel on steel, unless some of the conditions of the bath are changed.

Actual Run:

With the above characteristics in mind the first run was made. The 4" X 4" sheets of enameling iron used were cleaned in a cleaner solution for ten minutes, rinsed, and then pickled for five minutes.

They were then rinsed and singly placed in the nickel bath. The bath conditions were as follows:

2 Oz. single nickel salt per gal of water.

.25 oz. boric acid per gal of water.

pH- 6.2 plus or minus .1.

current density- 1.8 to 2 amp. per sq. ft.

temperature of bath- 164°F. down to 90°F.

voltage varied 2 to 3.4 volts, inverse as temp.

steel sheets 4" X 4".

anode-cathode distance 4.5 inches.

The time of immersion was varied from 2 to 6 minutes. The temperatures were 164, 150, 130, 110, and 90°F. After the sheets had been properly treated, they were rinsed, neutralized, and dried. A standard ground coat enamel was placed on the sheets by dipping. The weight of application was 1.125 oz. per square foot. The sheets were then fired out properly.

The adherence test was made by bending the corners of the enameled sheets over a wooden edge that had a radius of curvature of .25". Failure in adherence observed when bare steel was seen at the bend on the tension side . The angle through which the sheet had been bent to cause failure was measured and recorded. Identical sheets were enameled under the same conditions, except that the nickel coat was applied by galvanic action for five minutes. These galvanic sheets were given a rating of 10 because of their good adherence qualities. The electrolytic plated nickel sheets were rated in comparison with these galvanic sheets.

A re-run was carried out under the same conditions, except that the low temperature-short time and high temperature-long time portion of the series were omitted due to poor adherence in the first run. The temperature was increased to 180°F. as a maximum and lowered to 84°F. as a minimum. The maximum time was increased to 9 minutes at the lowest temperature. The same test of adherence was applied and again they were compared with sheets that had been galvanically nickel coated.

Results:

Temp. °F.	Time of immersion- minutes							
	2	3	4	5	6	7	8	9
180	4	5	6	7	6			
160		4	6	8	8	less than four		
140			6	6	10	8		
120	less than four			6	8	10	8	
100					10	8	7	
84					10	8	7	6

Enamel adherence to sheets given electrolytic nickel coat equals that of sheets given a galvanic coat when a rating of 10 is given, other values indicate proportionally inferior adherence.

From the data one can readily see that sheets which were electrically nickle coated under the experimental conditions at the temperatures of 140, 120, 100, and 84°F. for 6 and 7 minutes possessed the same enamel adherence qualities as sheets nickel coated in a galvanic bath at 170°F. for five minutes.

Conclusions:

Nickel applied to enameling steel or iron electrolytically from a nickel bath under the following conditions--

2 oz. single nickel salts per gal of water.
$\frac{1}{4}$ oz. boric acid per gal of water.
pH of solution- 6.2 plus or minus .1
temperature- 84 to 100°F.
time of immersion- 5 to 6 minutes.
cathode-anode distance- 4.5 inches.
monel metal tank-- 8" X 8" X 10"
sheets- 4" X 4"
current density- 2 amp/sq. ft.   voltage- 3.4

will cause enamelto adhere to the iron or steel to the same degree as nickel applied to enameling steel or iron galvanically under the following conditions--

2 Oz. single nickel salts per gal of water.
$\frac{1}{4}$ oz. boric acid per gal of water.
pH of solution- 5.6 to 6.4

temperature- 160 to 180°F.

time of immersion- 5 to 6 minutes.

tank, monel metal- 8" X 8" X 10"

sheets- 4" X 4"

As stated before, by calculations and experiment, a two minute deposit at 2 amperes per square foot current density and 170°F. deposits as much nickel as does the galvanic action from the same solution in five minutes. However, the results show that the best adherence is not obtained by a two minute deposit electrolytically which really is the equivalent of a five minute galvanic deposit. This may be explained by the fact that an electrolytic nickel deposit is tight, while a galvanic nickel deposit is a loose deposit which can actually be rubbed off. A loose deposit is more readily absorbed by the ground coat. For the enamel to take up an electolytic deposit, it appears that there must be more nickle available.

The author feels that much can be done on electrolytic nickel coating of enameling iron prior to enameling in an effect to equal the adherence produced by a galvanic coating of nickel.

-BIBIOGRAPHY-

Haessler, A.H., "Preparation of Metal Surfaces," A Manual Of Porcelain Enameling, Cleveland, Ohio, The Enamelist Publishing Company, 1937, p. 84.

Zander, J.M., "Trend Of Relation Between Nickel Deposit And Adherence," Better Enameling, Dec. 1940, p.10.

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