THE PERMEATION OF GASES THROUGH ELECTROLYTIC NICKEL DEPOSITS

Thesis for the Degree of Ph. D.
MICHIGAN STATE COLLEGE
J. Martin Tobin
1955

THE PERMEATION OF GASES THROUGH ELECTROLYTIC NICKEL DEPOSITS

By

J. Martin Tobin

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1955

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to the late Dr. Dwight Tarbell Ewing, under whose supervision and inspiration the experimental part of this thesis was accomplished before his death on August 5, 1954.

He is indebted to Dr. D. Gardner Foulke of Hanson-Van Winkle-Munning Company, whose clear insight into the problem was of invaluable aid in the organization of the program of research.

He is also greatly indebted to his major professor, Dr. Richard L. Bateman and to Dr. James L. Dye for their generous assistance in the construction of this thesis.

He expresses deep appreciation to the Hanson-Van Winkle-Munning Company of Matawan, New Jersey for a grant subsidizing this research.

* * *

ABSTRACT

The continuity of nickel electrodeposits is a very important factor limiting the corrosion protection afforded by nickel plating. In the absence of gross defects, it has been found that nickel electrodeposits are permeable to the flow of hydrogen and helium gases, which diffuse through a detached and mounted deposit along the intergranular boundaries. The permeability of the deposits to these gases is a measure of the extent of this type of discontinuity.

For the purpose of this investigation the nickel was deposited upon buffed nickel, from which it can be readily detached without disturbing the deposit. Samples of the detached deposit were mounted and placed in a high vacuum apparatus. The systems on both sides of the deposit were evacuated. Then, one atmosphere of either hydrogen or helium gas was admitted to the system on one side of the deposit. Gas flowed through the deposit under the difference of pressure and the pressure in the evacuated system was found to rise. The rate of pressure increase with time measures the permeation of the gas through the deposit.

The techniques involved in the production of deposits which were free from gross defects and of measuring the permeability of the deposits were developed to a point where reproducible results could be obtained.

Then, the effect of several variables in the deposition of nickel upon the permeability of the deposits were studied in order to determine the optimum conditions for the production of continuous deposits of nickel. The variables which were studied in the present investigation are the thickness of the deposit; the pH and the temperature of the plating bath; the cathodic current density; the concentration of the nickel salts and boric acid in the plating bath; the addition of organic compounds to the bath which tend to produce bright deposits; and, the addition of colloidal and metallic impurities to the bath.

In general, the addition of organic brighteners to the plating bath was found to decrease the permeability of the deposit. This was related to a definite difference in microstructure. The bright deposits were found to be fine grained and laminar in structure, while the dull deposits were quite granular in structure.

The permeability of the deposits was found to increase with higher bath temperature and cathodic current density, and with decrease in both the nickel salt and boric acid concentration in the plating bath. A very marked increase of about a thousand fold was obtained upon addition of metallic and colloidal impurities to the bath. The impurities in the plating bath have long been known to decrease the corrosion protection afforded by the deposit to the metal upon which it is plated.

The permeability of nickel deposits prepared by plating upon buffed nickel and upon buffed stainless steel were compared and found to be identical. This is probably related to the presence of the disoriented Beilby layer on both of the polished metals.

The most important effect which tended to increase the permeability of the deposits was the addition of both metallic and the colloidal impurities to the bath.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES - Continued Page

LIST OF FIGURES

FIGURE Page

I. INTRODUCTION

When a metal article is given a sufficiently thick coating of another metal, it can acquire the color, luster and corrosion resistance of the metal coating. In the field of electroplating, it has long been known that a "flash deposit" of a very few atoms thickness is sufficient to give an article the appearance of the deposited metal. However, a deposit of about sixty atoms thickness is required before the article develops the same electrochemical potential with respect to the plating bath that it would have if it were composed entirely of the pure deposit metal (1). Moreover, in the plating of steel parts with nickel, it has been found (2) that a deposit of at least one thousandth of an inch thickness of nickel is required before the steel article has a corrosion resistance comparable to that of pure nickel.

If the deposited metal were perfectly continuous, it seems that the deposit metal would dissolve uniformly in the presence of a corrosive medium. Actually, when a plated article is subjected to severe corrosion, the metal deposit is perforated through to the base metal at numerous discrete points. This type of corrosion is called "depth corrosion" and it usually takes place long before the actual thickness of the deposit is materially decreased by uniform dissolution in the corrosive medium.

For this reason, electrochemists have come to consider electrodeposited metals as quite discontinuous or porous. It is a common belief today that it takes at least one thousandth of an inch thickness of deposit before the pores or discontinuities beginning at the base metal are bridged over by the depositing metal (3).

In general, metal deposits may be classified as either anodic or cathodic coatings. Anodic coatings, such as zinc deposited upon iron, are so named because the metal coatings normally act as an anode in the presence of a corrosive medium and dissolve away in preference to base metal which is exposed through deposit discontinuities. The base metal in turn is cathodic with respect to the metal coating. Because of this sacrificial action, anodic coatings offer good corrosion protection despite deposit discontinuities.

Deposit discontinuities are much more important in the case of the cathodic coatings, such as nickel deposited upon steel, where exposed base metal is normally anodic and dissolves away in the presence of a corrosive medium. In fact, the base metal which is exposed through discontinuities in a cathodic coating can dissolve away at a much faster rate than if the coating were not present at all because of the shorted electrochemical cell which is set up in the presence of corrosive electrolytes. In order to obtain a maximum in corrosion protection, cathodic coatings must be as continuous as possible.

Electrodeposited nickel is the most important metal coating used for the protection of steel parts from the corrosive action of the outdoor atmosphere. It is used on all the "chrome" exterior decorations on automobiles, along with a very thin chromium deposit which improves its appearance. Because electrodeposited nickel occupies such a position of importance, the effects of several variables in the preparation of nickel deposits from various baths were investigated in order to determine the optimum conditions for the production of continuous deposits. The continuity of the deposits was determined by measuring the permeability of samples of detached nickel deposits to the flow of gases through the deposits.

The variables which were studied in the present investigation are the thickness of the deposit; the pH and the temperature of the plating bath; the cathodic current density; the concentration of the nickel salts and boric acid in the plating bath; the addition of organic compounds to the bath which tend to produce bright deposits; and, the addition of colloidal and metallic impurities to the bath.

II. HISTORICAL BACKGROUND

In an effort to understand the nature and causes of the pores or discontinuities in electrodeposited metal coatings, many porosity tests have been devised. Some of the tests have been quite popular, such as the salt-spray test, the ferroxyl test, and the hot-water test (4).

In the salt-spray test, the plated article or test panel is exposed to a very fine mist of air-saturated 3% NaCl solution until rust spots appear and show the presence of the pores. It is an "accelerated corrosion" test.

In a convenient modification of the ferroxyl test, a filter paper is saturated with a solution of sodium chloride and potassium ferrocyanide. When the filter paper is applied to a clean plated surface a number of spots appear on the paper in a short time. If the base metal is steel, the spots are colored blue.

The simplest test is the hot-water test. It consists of submerging the article or panel in boiling water and observing the formation of rust spots.

These tests suffer from the disadvantage that the tests are not well enough understood to be interpreted in terms of the nature and causes of the pores except in a very qualitative manner. Their main usefulness lies in their ability to predict with reasonable accuracy the corrosion resistance of the deposit and the service life of the plated article.

After World War II, government regulations on the use of nickel limited the amount of nickel available for decorative purposes. In order to obtain the greatest corrosion protection with a limited thickness of nickel it became more important that the nickel be deposited in a very continuous manner.

The American Electroplaters' Society organized a research project, A.E.S. Project 6, in the year 1946 for the purpose of studying porosity of electrodeposited metals. The director of the project was the late Dr. Nathaniel Thon of Princeton University. Dr. Thon published a series of thirteen papers before his death in 1953.

The first paper of the series (5) consists of a bibliography of 226 technical papers concerned with porosity of electrodeposited metals and tests for that porosity. In the second paper (1) he critically reviews the previously published articles and evaluates the chemical and physical tests used.

The third paper (6) deals with the measurement of intrinsic porosity of detached electrodeposits. He defines intrinsic porosity as that porosity present in even perfect deposits because of voids between the crystals or grains. The first method he used for determining the intrinsic porosity of a deposit is the measurement of the time required for a small difference in pressure across a detached and mounted deposit to fall to one-half of its original value. However, this method was not sensitive enough to measure the intrinsic porosities, which were much lower than expected.

The fourth paper (7) of the series describes a more sensitive method which he calls the low pressure-constant overpressure method. If the system on one side of the detached and mounted deposit is evacuated and there is an atmosphere of pressure on the other side, gas will flow through the deposit at an easily measureable rate. The difference in pressure across the deposit, which is defined as the overpressure, is then essentially constant. The permeability of the deposit to gas, as measured by the rate of flow of gas, is a quantitative measure of the porosity of the deposit. And, if the deposit is free from gross defects such as gas pits, the permeability is called the intrinsic permeability. The intrinsic permeability is a physical characteristic of the deposit which is dependent upon its microstructure.

When the latter method was applied to different areas of the same deposit, however, the results varied by a factor of a thousand. Subsequent papers dealt with improved deposit mounting (8); various methods of detaching the deposit (9); correlation of permeability to base metal surface roughness (10); variation of the overpressure used (8); increase of permeability with exposure to corrosive media (11); analysis of corrosion products from plated articles (12); and, estimation of the total surface area of the deposit by the Brunauer, Emmett and Teller method (13).

Unfortunately, Dr. Thon's research was interrupted by his death before he was able to develop the method of measuring the permeability to the point where reproducible results could be obtained.

Another research project of the American Electroplaters' Society is the A.E.S. Project 13, under the direction of Fielding Ogburn of the National Bureau of Standards. The purpose of Project 13 is the study of the nature, cause and effect of the porosity in electrodeposits. In an article recently published by that group (14), they report the results of measuring the effect of corrosion upon the permeability of nickel electrodeposits to gas. They find the gas permeability measurements as obtained by the above method to be unsatisfactory and suggest another porosity test which they have developed. A detached deposit is placed on a plate of glass. A piece of commercial contrast film is placed on the other side of the glass. Then, the whole is properly masked from light so that the only light which can affect the film is that which passes through the deposit. The deposit is then exposed for a long time to light. When the film is developed, dark spots appear where light has passed through pores in the deposit. Those pores which pass light through the deposit are called photographable pores by the authors.

Both a modification of the low pressure-constant overpressure method and the photographic method were used in the present investigation.

III. APPARATUS AND PROCEDURE

Apparatus

The apparatus used in this investigation for the measurement of permeability by the low pressure-constant overpressure method is very similar in principle to the ones used by Thon (6) and Ogburn (14). A picture of the apparatus is given in Figure 1. The apparatus is constructed almost entirely of glass.

Two other apparati have been built in this laboratory by Russell Fay for studying the diffusion of gases through metals. The first was used to determine the effect of corrosion upon the gas permeability and the second for the study of the effect of large changes in the overpressure used. These apparati are described in Fay's thesis (15).

The experience gained in the use of the first two apparati showed that a few improvements in the construction of the new apparatus would be helpful in reducing the systematic errors involved in the permeability measurements. These changes are described below.

There are three interconnecting glass systems which comprise the whole apparatus, a) the gas source system, b) the evacuation system, and c) the permeation system. A schematic diagram of the three systems is given in Figure 2.

The gas source systems of the old apparati were meant to supply dry air for permeation and for adjusting pressures in other parts of the apparati. Each was simply a train of two drying columns and a capillary

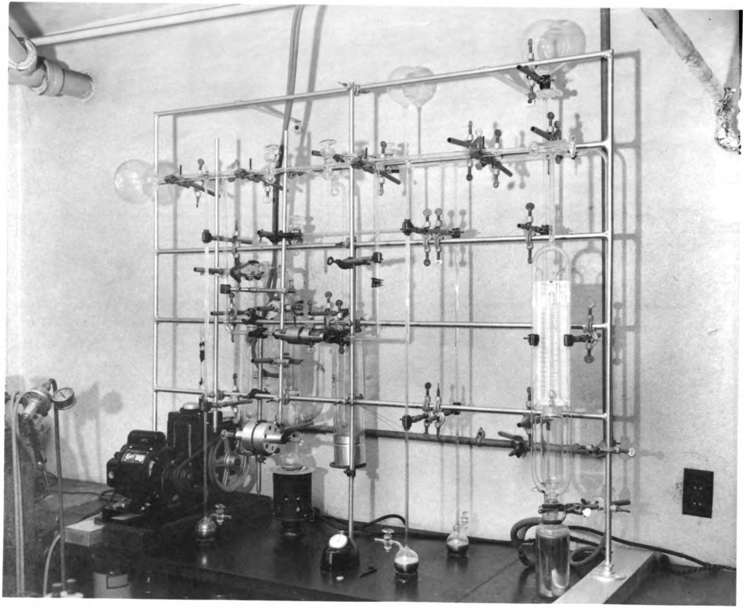

Figure 1. A photograph of the apparatus.

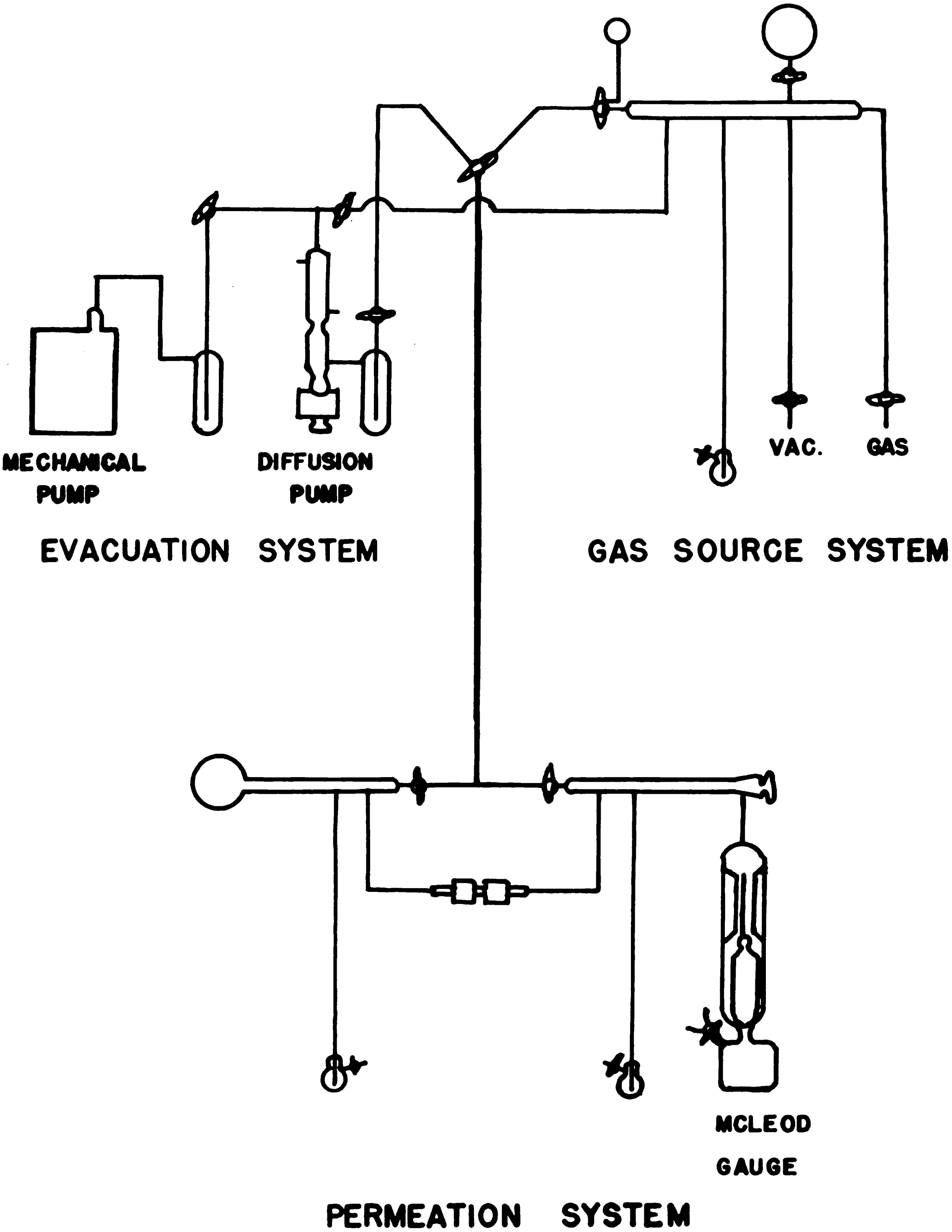

Figure 2. A schematic diagram of the apparatus.

tube for restricting the flow of the air. However, they did not serve their purpose well as the water content of the air they delivered was not only high, but varied considerably. This was evidenced by the length of time required to establish a very high vacuum after the system had been exposed to the air. Compressed gas from tanks is used in the new apparatus because the composition is quite constant. A manometer is used to regulate the flow of gas accurately and decrease the strain on the mounted deposit which is caused when an overpressure is being established across the deposit. The means of evacuation shown in the diagram is necessary because of the number of different gases which are used in the apparatus. One gas must be removed from the system before another is introduced.

Two changes in the evacuating system were found necessary in the new apparatus. A cold-trap was introduced between the Cenco Hypervac 4 vacuum pump and the single throat mercury diffusion pump, greatly reducing the contamination of the vacuum pump oil with mercury. A large bore stopcock has been placed between the two pumps in order to disconnect the apparatus from the mechanical pump when detecting leaks.

The permeation system itself consists of two parts separated by the mounted nickel deposit, the high vacuum side and the overpressure side. The high vacuum side of the new apparatus has a very sensitive double-scale McLeod gauge and a manometer, giving a range of pressure readings from 10^{-6} mm. to 780 mm.

A very important part of the apparatus is the aluminum cell which holds the mounted deposit. It was developed by Russell Fay and is described in his thesis (15). A picture of the cell is given in Figure 3. The cell has been separated in order to show the cavity in which a mounted deposit is placed. The parts used in mounting the deposit are shown in the foreground. A circular disc of the deposit is mounted between two annular rings of "Lucite" plastic and sealed with Cenco Tackiwax. The two annular black rings are gaskets made of outgassed Buna S rubber.

Another manometer is used to determine the pressure in the overpressure side of the permeation system.

Procedure

a. Preparation of the detached deposits.

It is important that the deposits be carefully prepared as the permeability test is so sensitive. The permeability of a sample of a deposit which contained a very small photographable pore was found to be a thousand times greater than that of five other samples taken from the same deposit. The values for the other five were identical. This comparison was repeated several times and in each case the permeability of the deposit sample which contained the photographable pore was much greater than that of samples of the same deposit which did not contain photographable pores. When a very small piece of high vacuum wax was applied to a photographable pore, using a microscope and transmitted light to find the pore, the permeability was then found to be identical with the others from the same deposit. For this reason, each deposit was tested for photographable pores by the method described before, and those deposits which contained them were discarded.

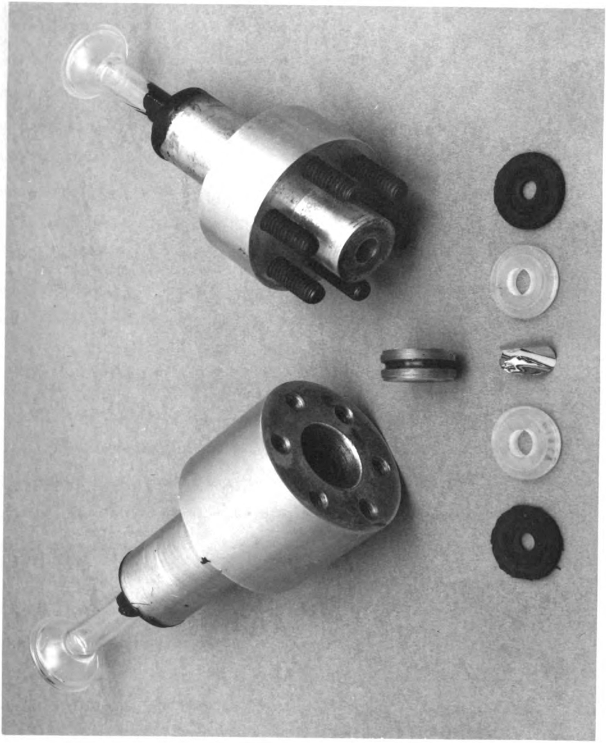

Figure 3. A photograph of the aluminum cell.

Sometimes the permeability of a sample of a deposit was found to be unusually high and a photographable pore could not be detected. In those cases, it was always possible to find a pit or scratch in the surface of the base metal under that part of the deposit using a thirty-five power binocular microscope. Deposit defects of this type were eliminated by carefully examining the base metal panels with a microscope before the preparation of a deposit and rejecting the panels with pits or scratches on their surface.

The plating baths used in the preparation of the deposits were freshly prepared, purified and filtered. The purification procedure used was that recommended by the American Electroplaters' Society Research Project 5 (16). The first step in the procedure involved adding 1 cc. of hydrogen peroxide (3%) and about 5 grams of nickel carbonate per liter of bath. When the bath was allowed to stand overnight in the presence of the insoluble nickel carbonate, the pH of the bath would rise and the hydroxides of several metal impurities, notably iron, precipitated from the bath. The excess nickel carbonate and the precipitated hydroxides were filtered from the bath the next day. About 5 grams per liter of activated carbon (Norit A) were added to the filtered bath and the bath was heated to its boiling point for two hours. The purpose of this step in the procedure is to decompose the hydrogen peroxide remaining in the bath, expel the dissolved carbon dioxide and adsorb organic impurities from the bath upon the activated carbon. The bath was then filtered and its pH was lowered to a value of 2.2 using a few drops of concentrated sulfuric acid. The bath was then electrolyzed at a low cathodic current density of 5 amps per square foot of cathode surface area for one hundred ampere hours. During the electrolysis, heavy metal impurities in the bath were reduced to a few parts per million (16). The bath was then filtered and stored in glass bottles.

The base metal panels used in the preparation of the detached deposits were prepared by plating pieces of 0.010 inch thick steel shim stock measuring about 2.5 by 3 inches with nickel from a Watts type bath of the following composition:

Nickel sulfate	240 grams/liter
Nickel chloride	45 grams/liter
Boric acid	30 grams/liter
pH range	2.2 to 5.2

They were buffed to a very smooth, bright finish using Acme Pink Finish produced by Hanson-Van Winkle-Munning Company. The thickness of the nickel plate on the base metal was about 0.001 inch thick.

In order to prepare an easily detached deposit, the base metal was treated in the following manner in an effort to produce a uniform, passive film on its surface. The panel was wiped with a cheesecloth soaked in ethyl alcohol to remove most of the buffing compound. Then it was oxidized for five minutes at the anode in an alkaline electrolytic cleaning bath of the following composition:

Sodium hydroxide	21 grams/liter
Sodium metasilicate	15 grams/liter
Trisodium phosphate	18 grams/liter
Sodium carbonate	6 grams/liter

The temperature of the bath was 90 to 95°C and the anodic current density was 80 amps per square foot. Next, the panel was dipped into 20 per cent (by volume) hydrochloric acid solution for 20 seconds, oxidized at the anode in the cleaning bath for 20 seconds, dipped into the 20 per cent hydrochloric acid for 5 seconds, and then rinsed with distilled water. The panel was introduced into the plating bath while it was still wet.

The deposition of the nickel for the permeation studies was carried out under controlled conditions of temperature, cathodic current density, and stirring. During deposition, gas bubbles which adhered to the panel were released by striking the panel. This method was very successful in reducing the number of photographable pores. In fact, there was no difficulty in producing deposits without any photographable pores.

When the deposit had reached the desired thickness, as determined from its known rate of deposition, the current was turned off and the panel was removed from the bath. The plating solution was rinsed from the panel with distilled water made up to the same pH as that of the plating bath with sulfuric acid. The distilled water was acidified in order to eliminate the possibility of precipitation of basic nickel compounds within the pores of the deposit. When the panel was dry, four cuts were made through the nickel deposit with a razor blade about one quarter of an inch from the sides of the panel. Then, a rectangular area two by two and a half inches of the nickel deposit could be easily lifted from the base metal panel. The detached deposit panel was then marked for identification.

The numbering system is shown in Figure 4. In the identification code number for a sample taken from a deposit panel, such as sample B12C-2C, the letters and number preceding the hyphen designate the

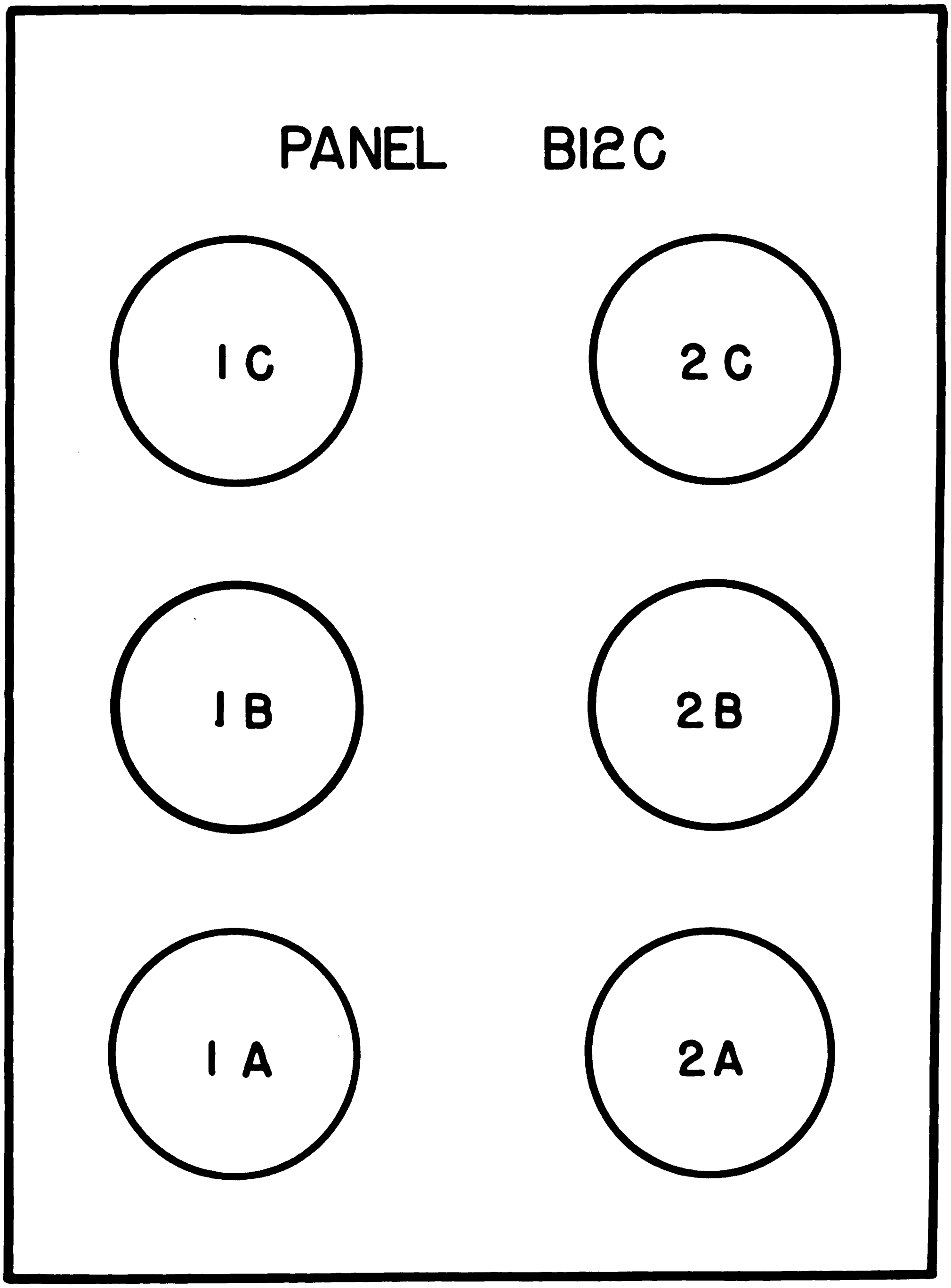

Figure 4. An illustration of the numbering system.

deposit panel from which the sample was taken. The first letter is a symbol designating the plating bath which was used. The number identifies the base metal panel which was used. The following letter is interpreted as the deposit number from that particular panel.

After the deposit panel was tested for the presence of photographable pores, six circular samples of five eighths inch diameter were cut from the panel using a steel die punch. The only part of the sample which was affected by the punch was the circumference of the area. A number and a letter were assigned to each sample showing the position from which it was taken from the deposit panel. They follow the hyphen in the sample identification code. The samples were marked near the circumference with their code number, after the sample was weighed.

The deposit samples were dried in a vacuum dessicator and weighed on a semi-micro analytical balance. The mean thickness of the deposit sample was found by assuming the density of the deposit to be about 8.90 grams/cubic centimeter (17). The area of the samples was 1.96 square centimeters. An example of the calculation of the thickness of a deposit weighing 0.00450 grams is as follows:

$$\text{thickness (cm.)} = \frac{4.50 \times 10^{-3}\ \text{g.}}{1.96\ \text{cm.}^2 \times 8.90\ \text{g/cm.}^3}$$

$$= 2.61 \times 10^{-4}\,\text{cm.}$$

$$= 1.02 \times 10^{-4}\,\text{inch}$$

The deposit samples were then mounted between two annular rings of "Lucite" plastic. One surface of each ring was lapped to a smooth, flat surface on a plate of glass using 1000 grit silicon carbide abrasive. A channel was provided in the rings so that the mounted sample could be sealed tight with vacuum wax. The outside diameter of the rings was three quarters of an inch and the inside diameter was one quarter of an inch. The inside diameter of the rings determined the area of the deposit which was measured for its permeability. The exposed area of the deposit measured was 0.375 square centimeters.

The mounted deposit samples were stored at room temperature in an evacuated vacuum dessicator.

b. Measurement of the permeability of the nickel deposits to gases.

The nickel deposits which were studied in this investigation were found to be relatively impervious to the flow of air or nitrogen through the deposit. However, when hydrogen and helium gases were used as the permeating gases, measureable rates of flow were obtained.

The increase in pressure in the evacuated part of the permeation system, the high vacuum side, was used to measure the rate of flow of gases through the deposit. However, the total increase in pressure in the high vacuum side was only partly caused by the flow of gas through the deposit. The increase in pressure which was caused by the flow of gas through the deposit was of the same order of magnitude as the increase in pressure caused by other effects.

One of these effects was the desorption of gases from the walls of the system. This effect was not entirely eliminated but it was controlled by the use of gases from tanks rather than air.

The other effect of importance was the evolution of dissolved or occluded gases from the nickel deposit. This second effect can be very large for a freshly deposited sample. The amount of dissolved or occluded gases in a freshly deposited sample of nickel from a Watt's type bath at a pH of 2.2 (0.000525 inch thick) was determined in the following manner. The rate of evolution of gas from the mounted deposit was followed at the rate of pressure increase per unit of time. The permeation system was evacuated at 25°C and a constant pressure of one micron for 4200 minutes. The rate of evolution of gas was measured occasionally by separating the permeation system from the evacuation system for a few minutes and recording the rise in pressure per unit of time. Correction was made for that part of the pressure increase caused by desorption of gas from the walls of the system by testing an out-gassed deposit in exactly the same manner. However, the second deposit sample was previously stored for several days in an evacuated vacuum dessicator to remove dissolved and occluded gases.

The data which were taken are listed in Table I. A graph of the rate of pressure increase as a function of the time of evacuation at constant temperature and pressure is shown in Figure 5. The area between the curve obtained from the fresh deposit and the curve obtained from the out-gassed deposit was obtained by graphical integration, and is approximately 22 microns or 3.4×10^{-5} atmosphere. The volume of the high vacuum side was determined by allowing gas at a measured pressure in a small calibration bulb of a definite volume to expand into the high vacuum side and applying the perfect gas law. Then, from the known volume of the high vacuum side and the temperature, the number of moles of evolved gas can be calculated.

TABLE I

DATA SHOWING THE DIFFERENCE IN VAPOR CONTENT OF FRESH AND OUTGASSED NICKEL DEPOSITS

Time of Evacuation at Constant Pressure (Minutes)	Rate of Pressure Increase In the Closed System (Microns/Minute)
Fresh Deposit	
60	0.458
90	0.387
240	0.343
360	0.300
480	0.269
600	0.234
720	0.210
840	0.191
960	0.166
1080	0.148
1200	0.135
1320	0.120
1800	0.0707
2400	0.0444
2880	0.0206
3600	0.0087
4200	0.0038
Out-Gased Deposit	
60	0.115
90	0.0672
150	0.0374
240	0.0219
600	0.0031
1200	0.0013

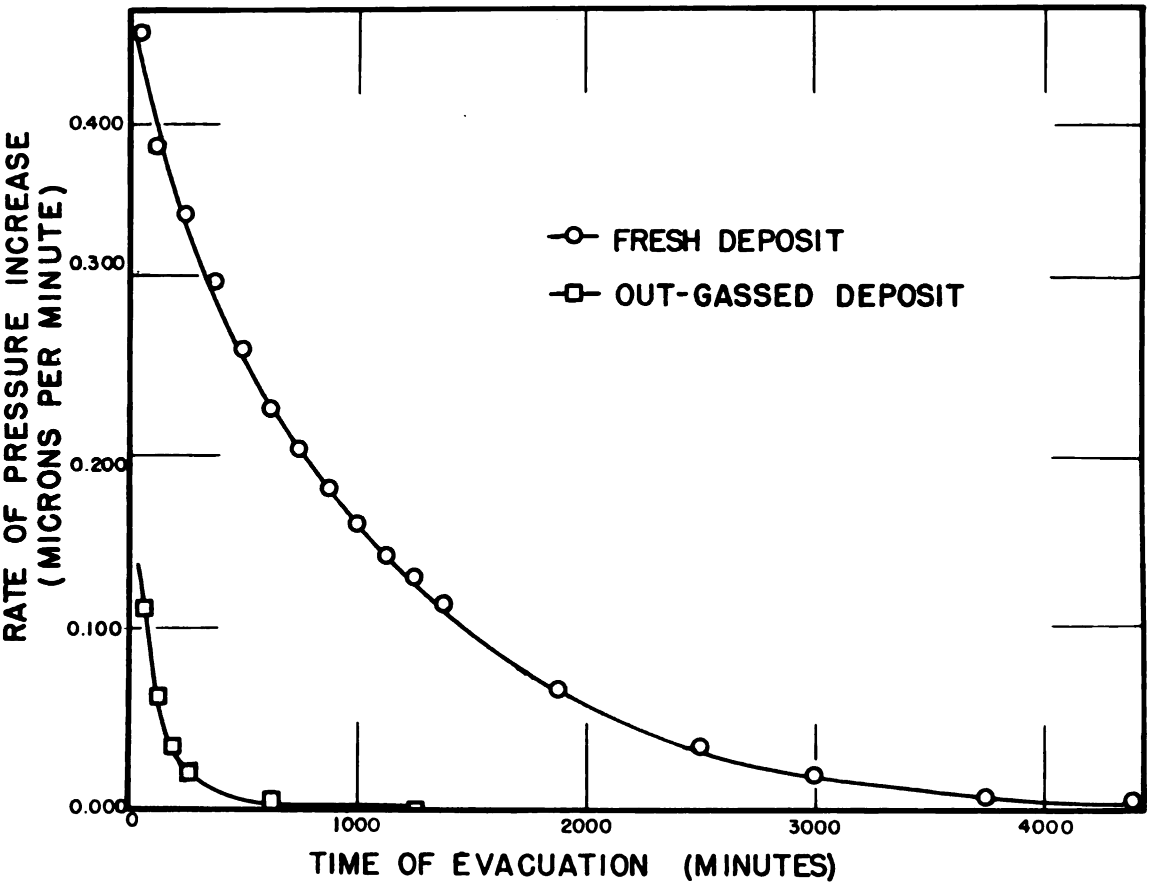

Figure 5. A graph showing the rate of escape of vapor from a fresh deposit with time of evacuation.

$$n = \frac{PV}{RT} = \text{number of moles of evolved gas}$$

$$= \frac{3.40 \times 10^{-5} \text{ atmos.} \times 1.45 \text{ liters}}{8.20 \ \frac{\text{liter-atmos.}}{\text{mole-degree}} \times 298 \text{ degrees}}$$

$$= 2.02 \times 10^{-8} \text{ moles}$$

A very simple qualitative test to determine the proportion of the pressure indicated by a McLeod gauge which is due to vapor is to cool the capillary tip of the gauge. In the McLeod gauge, the absolute pressure of the gas in the tip of the capillary is approximately equal to the difference in height of the two mercury columns, and may be easily measured in millimeters of mercury of pressure. When the tip is cooled, the vapors in the tip condense and the pressure indicated by the gauge is that caused by the permanent gases. When the tip was cooled after out-gassing a fresh deposit into the high vacuum, most of the gas given off by the deposit was found to be a vapor, presumably water vapor.

Assuming the gas to be all water vapor, the percent of water in the deposit was calculated as follows:

$$\text{Percent } H_2O = \frac{\text{Wt. } H_2O \times 100}{\text{Wt. Ni}}$$

$$= \frac{2.02 \times 10^{-8} \times 18.0 \times 10^{2} \text{ grams}}{\frac{0.375 \text{ cm.}^2}{1.96 \text{ cm.}^2} \times 0.02362 \text{ grams}}$$

$$= 0.00809\%$$

The low pressure-constant overpressure method developed by Thon was modified in the following manner in order to correct for the effects mentioned above and obtain the increase in pressure in the high vacuum side which was caused by permeation of gas through the deposit alone.

The deposit samples were out-gassed by evacuation for several days in a vacuum dessicator. Then the mounted sample was placed in the aluminum holder in the permeation system of the apparatus. The permeation system was evacuated at the maximum speed of both the mechanical and diffusion pumps for five hours.

The permeation system was then shut off from the rest of the apparatus. The pressure in the high vacuum side of the system was found to rise in a manner dependent upon which gas had been used in the permeation system before evacuation and also dependent upon the time of evacuation. Since the overpressure side was also evacuated, there was no difference in pressure across the deposit and no flow of gas occurred through the deposit.

Data were taken of the rise in absolute pressure as a function of time and a curve was established showing the combined effects of desorption from the glass walls and the out-gassing from the deposit. The curve was found to be essentially linear in the range which was studied. A typical curve is shown in Figure 6. In this case, there had been helium gas in the system and the time of evacuation was five hours.

When gas was admitted from the gas source system to the overpressure side of the permeation system till the overpressure reached one atmosphere, a sharp inflection occurred in the curve. This can be seen in Figure 8. The increase in the rate of pressure rise is caused by gas permeating through the deposit. It is equal to the difference between the slopes of the two curves. Although the rate is actually measured

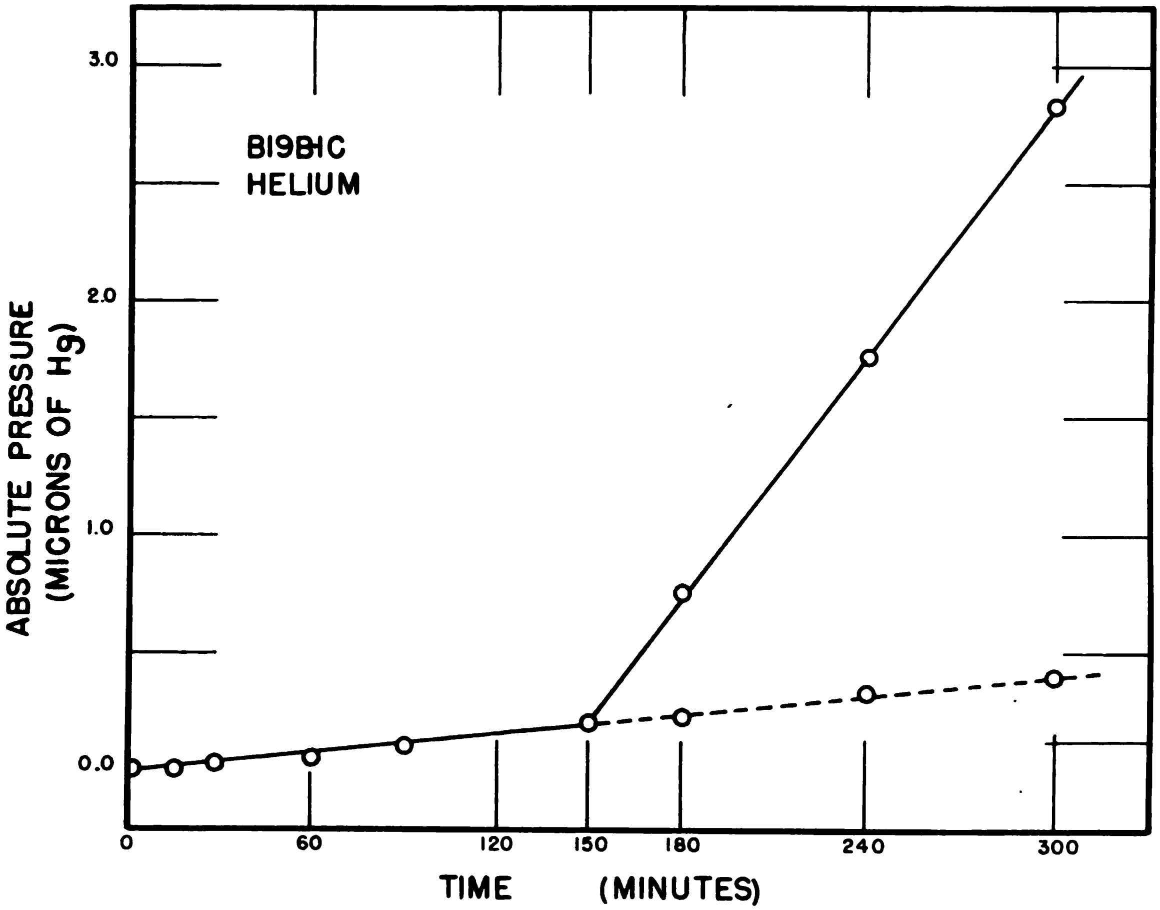

Figure 6. A graph illustrating the method used to eliminate several systematic errors from the permeability measurements.

in microns per minute, it is converted to millimeters per minute, the units used by Dr. Thon. The conversion factor is one thousand microns per millimeter.

A permeability constant, k, has been defined by Dr. Thon (7) which is independent of the overpressure over a large range of overpressures (8). Although the overpressure used in all the measurements in this investigation was one atmosphere, the permeability constants were calculated so that the results of the present investigation may be compared with those of other workers in the same field using different values of overpressure.

The equation developed by Dr. Thon and the meanings of the terms in the equation are shown in Figure 7.

Using the procedure described above for the preparation of the detached deposits and the measurement of their permeability constants, reproducible values of the permeability constants were obtained.

Figure 7.

DEFINITION OF THE PERMEABILITY CONSTANT, K

When the overpressure is a large and constant value, e.g. one atmosphere, a permeability constant is defined by Thon* as follows:

$$K \; \frac{\text{liters}}{\text{cm.}^2\ \text{min.}} = \frac{V}{F} \; \frac{\text{liters}}{\text{cm.}^2} \times \frac{1}{P} \; \frac{1}{(\text{mm.})} \times \frac{\Delta P}{\Delta T} \; \frac{(\text{mm.})}{(\text{min.})}$$

V = Volume of the vacuum system on one side of deposit
= 1.45 liters
F = Area of the deposit being measured
= 0.375 cm. square
P = Overpressure in mm. of Hg
= 760 mm.
ΔP = Change of pressure in the evacuated system in mm. of Hg
Δt = Time interval in minutes

Thus, if the overpressure is kept constant for a series of foils, the ratio of the permeability constants is the same as the ratio of the rates of diffusion.

* Thon, Kelemen and Yang, Plating, 36, 362-6 (1949)

IV. RESULTS

The intrinsic permeability of detached nickel electrodeposits was found to be dependent upon many variables. The ones which were studied were the thickness of the deposit; the pH and temperature of the plating bath; the cathodic current density; the concentration of the nickel salts and boric acid in the plating bath; addition of organic compounds to the bath which tend to produce bright deposits; the addition of colloidal and metallic impurities to the bath; and, the base metal which is used.

Thickness of the Deposit

Of all the variables involved in the electrodeposition of nickel, the one which is recognized to be the most important by electroplaters is the thickness of the deposit. The thicker the deposit, the greater the corrosion protection afforded by the deposit. The minimum thickness of the deposit is always specified in those applications where corrosion protection is important.

Four series of deposit samples were prepared of about 0.0005, 0.0002, 0.0001, and 0.00005 inch thickness respectively. They were the B16A, B16B, B19A and B19B series. The four panels were prepared from a Watts type bath (refer to page 15) at a pH of 2.2, and a temperature of 60°C. The cathodic current density was 40 amps per square foot.

The rates of flow of helium through the deposit samples with one atmosphere of overpressure were measured. Values of the permeability constants were calculated from the rates of flow and are listed in Table II.

TABLE II

DATA SHOWING THE EFFECT OF DEPOSIT THICKNESS UPON THE PERMEABILITY

Deposit Sample	Mean Thickness (in.)	Inverse Mean Thickness (10^4 in.$^{-1}$)	$K_{H_2} \times 10^8$ (l./cm.^{2}min.)	K_{N_2}	$K_{He} \times 10^8$ (l./cm.^{2}min.)
B16A-1A	0.00055	0.18	---	(0)	2.2
B16A-1B	0.00051	0.20	---	(0)	2.4
B16A-1C	0.00047	0.21	---	(0)	2.4
B16A-2A	0.00057	0.18	---	(0)	2.3
B16A-2B	0.00053	0.19	---	(0)	2.3
B16A-2C	0.00048	0.21	---	(0)	2.5
B16B-1A	0.00022	0.45	---	(0)	4.3
B16B-1B	0.00021	0.48	---	(0)	4.5
B16B-1C	0.00020	0.50	---	(0)	4.6
B16B-2A	0.00024	0.42	---	(0)	4.0
B16B-2B	0.00021	0.48	---	(0)	4.6
B16B-2C	0.00019	0.53	---	(0)	4.7
B19A-1A	0.000107	0.93	8.7	(0)	6.1
B19A-1B	0.000102	0.98	9.0	(0)	6.3
B19A-1C	0.000096	1.04	9.2	(0)	6.5
B19A-2A	0.000115	0.87	8.5	(0)	5.9
B19A-2B	0.000099	1.01	8.9	(0)	6.5
B19A-2C	0.000093	1.08	9.4	(0)	6.7
B19B-1A	0.000053	1.88	---	(0)	8.1
B19B-1B	0.000049	2.06	---	(0)	8.2
B19B-1C	0.000045	2.22	---	(0)	8.3
B19B-2A	0.000055	1.80	---	(0)	8.0
B19B-2B	0.000051	1.97	---	(0)	8.2
B19B-2C	0.000044	2.28	---	(0)	8.4

Note: The rates of flow of nitrogen through these deposits is less than the accuracy of reading the McLeod gauge.

The k values for nitrogen gas are listed as zero because the rate of flow of this gas through the deposit is less than the error involved in reading the McLeod gauge, however, the measurements were always on the positive side of values at no overpressure and there might have been some flow of the gas.

The permeability of the B19A series of deposit samples to hydrogen gas with one atmosphere overpressure was also measured for the sake of comparison with other deposits described later. The thickness of the B19A series was approximately 0.0001 inch, and this thickness of deposit was used in all the subsequent studies.

According to Barrer (18), if a porous material is uniform throughout its thickness, the permeability of the material is inversely proportional to its thickness. This is a very general rule and has been well established for numerous substances, including nickel foils prepared by casting and hot rolling.

However, the permeability of nickel deposits from a Watts type bath at a pH of 2.2 is not inversely proportional to the thickness of the deposit. This can be seen in the graph shown in Figure 8, where the permeability constant for helium gas is plotted as a function of the reciprocal thickness. Apparently, as the nickel is deposited, the metal which is being deposited becomes less porous as the thickness of the deposit increases. Although it is possible that the curvature is caused by a systematic error, it doesn't seem probable because the slope obtained from the points internal to a particular group of samples definitely changes in a regular fashion from group to group.

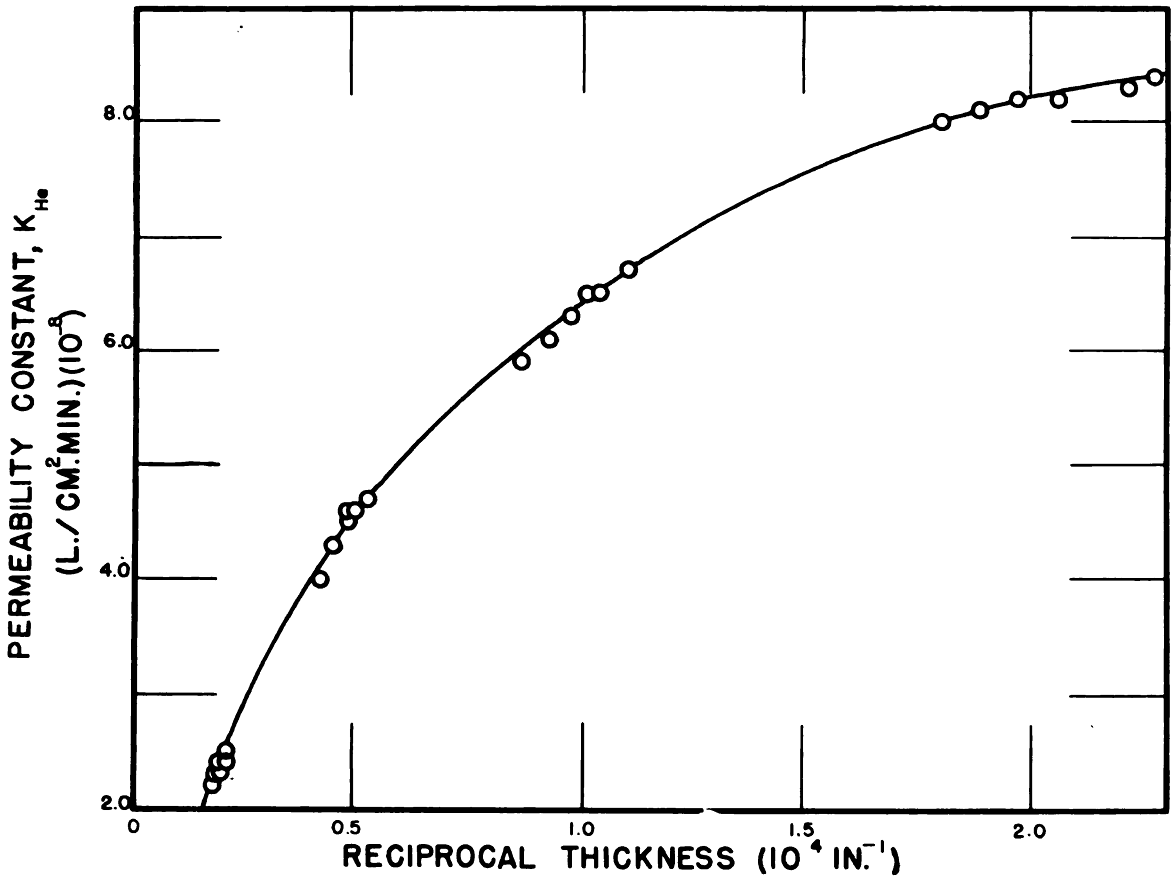

Figure 8. A graph showing the effect of deposit thickness upon the permeability.

Metallographic studies by Brenner et al. (19) show that, in general, the grain size of a deposit from a Watts type bath increases with thickness. As the grain size increases, the grain boundary surface decreases, and there are fewer channels for grain boundary diffusion of gas through the deposit.

This was the first indication that the process by which the gas flows through the electrodeposited nickel is by grain boundary diffusion.

Another indication was the relatively higher permeability of the nickel electrodeposits as compared to the permeability of rolled nickel of about the same thickness (7). Although hydrogen, nitrogen and oxygen will diffuse through rolled nickel, either an overpressure of several hundred atmospheres must be used at room temperature or a temperature of several hundred degrees must be used at low overpressures. Even at high temperatures and pressures helium doesn't diffuse through rolled nickel (20), primarily because it is a chemically inert gas. The other gases diffuse through rolled nickel either by solution diffusion or by interstitial lattice diffusion.

Solution diffusion and lattice diffusion are called volume diffusion processes and are independent of the micro-structure. Grain boundary diffusion is a structure sensitive diffusion, which makes it such a useful tool in the present application. These diffusion processes may take place simultaneously, but the solution diffusion and lattice diffusion processes have such a high activation energy that they are negligible at lower temperatures and pressures compared to the grain boundary diffusion process. Since the velocity of diffusion in the case of the volume diffusion processes is largely governed by the exponential term in the equation

$$D = D_0 e^{-E/RT}, \qquad (21)$$

the velocity of grain boundary diffusion may exceed that of volume diffusion even though the number of paths available for lattice diffusion and solution diffusion is much greater than the number of paths available for grain boundary diffusion.

In order to prove that the predominant process of diffusion through nickel electrodeposits is grain boundary diffusion, a comparison was made between the rates of flow of hydrogen and helium through twelve deposit samples. The B19A series and the B30B series were used.

According to Graham's Law, the ratio of the rates of flow of two gases through a small orifice in a thin plane wall is equal to the square root of the inverse ratio of their molecular weights. This method is sometimes used to determine the molecular weight of an unassociated gas (22).

The ratios of the rates of flow for the two gases have been calculated and are listed in Table III. The mean value of the ratio is 1.42, which compares favorably with the value 1.41 found by Graham's Law. The agreement with Graham's Law shows that the gases diffuse through the deposit by way of capillaries, the grain boundaries. According to Barrer (22), the size of the capillaries must be small compared to the mean free path of the gas molecules. Since an atmosphere of overpressure was used, the atoms of helium at one atmosphere, for instance,

TABLE III

DATA SHOWING THE AGREEMENT OF EXPERIMENTAL RATES OF FLOW WITH GRAHAM'S LAW

From Graham's Law:

$$\frac{K_{H_2}}{K_{He}} = \sqrt{\frac{M_{He}}{M_{H_2}}}$$

$$= 1.41$$

(If both K values are obtained at the same temperature and overpressure.)

Deposit Sample	$\frac{K_{H_2}}{K_{He}}$
B30B-1A	1.43
B30B-1B	1.41
B30B-1C	1.43
B30B-2A	1.41
B30B-2B	1.41
B30B-2C	1.50
B19A-1A	1.43
B19A-1B	1.43
B19A-1C	1.41
B19A-2A	1.44
B19A-2B	1.37
B19A-2C	1.40
Mean Value	1.42

travel about 1000 Å on the average before they collide with another atom. If the diameter of the hole in the thin wall is small in comparison with the mean free path, then an atom on reaching the opening is unlikely to collide with another atom but will pass right through. It follows then that the number of molecules passing through the orifice is almost equal to the number which would normally strike an area of wall equal to that of the hole, which is inversely proportional to the molecular weight of the gas.

Thus, the intrinsic permeability of the nickel electrodeposits was found to be caused by diffusion along the grain boundaries which are very fine and probably very numerous.

The pH of the Plating Bath

The Watts type nickel plating bath is commonly used at various values of pH from 2.2 to 5.2. At lower pH values, codeposition of hydrogen is excessive and the deposit may be seriously pitted. When a bubble of hydrogen becomes attached to the cathode, the electrical field in the solution is distorted so that no nickel deposits at the site of the attached bubbles. This gives rise to large gas pits in the deposit.

At pH values higher than 5.2, basic nickel compounds tend to precipitate in the layer of solution adjacent to the cathode whose pH is ordinarily higher than that of the main body of the solution. The basic nickel compounds are occluded in the deposit and render it unsatisfactory in appearance and mechanical properties.

Three series of deposit samples were prepared using a Watts type bath at a temperature of 55°C and at three pH values of 2.2, 3.2 and 5.2.

They were the G3LA, C21A, and D21B series respectively. The cathodic current density was 40 amps per square foot.

The permeability of the six deposit samples in each series was measured using hydrogen and helium at one atmosphere of overpressure. The permeability constants were calculated from the rates of flow and are listed in Table IV. The thickness of the deposit samples was about 0.0001 inch.

It can be seen from the table that the pH of the plating bath does not have a very large effect upon the permeability of the nickel deposits to gases, at least in the range which was studied. Apparently, the microstructure of the deposit changes very little upon increasing the pH from 2.2 to 5.2. This observation is in excellent accord with the findings of other investigators (19).

Temperature of the Plating Bath

Most nickel plating baths are used in the temperature range of 50 to 60°C. Higher temperatures are sometimes used in order to increase the speed of production of plated articles. At higher temperatures, more nickel salt can be dissolved in the bath, the bath becomes less viscous and the ionic mobilities increase. These factors enable the electroplater to use a higher current density and obtain faster deposition. However, there are several disadvantages. Perhaps the most important is the decrease in corrosion protection afforded by the deposit to the base metal.

A Watts type bath at a pH of 2.2 was chosen for the study of the effect of the temperature of the plating bath upon the permeability of

TABLE IV

DATA SHOWING THE EFFECT OF pH OF THE PLATING BATH UPON THE PERMEABILITY

Deposit Sample	Mean Thickness (in.)	$K_{H_2} \times 10^8$ (l./cm.^{2}min.)	K_{N_2}	$K_{He} \times 10^8$ (l./cm.^{2} min.)
		pH = 2.2		
G31A-1A	0.000126	8.60	(0)	6.05
G31A-1B	0.000122	8.70	(0)	6.15
G31A-1C	0.000104	8.95	(0)	6.40
G31A-2A	0.000142	8.65	(0)	6.00
G31A-2B	0.000125	8.85	(0)	6.25
G31A-2C	0.000113	9.00	(0)	6.30
		pH = 3.2		
C21A-1A	0.000110	14.2	(0)	10.2
C21A-1B	0.000103	14.5	(0)	10.5
C21A-1C	0.000097	----	(0)	----
C21A-2A	0.000120	14.0	(0)	10.0
C21A-2B	0.000104	14.5	(0)	10.5
C21A-2C	0.000099	15.5	(0)	11.0
		pH = 5.2		
D21B-1A	0.000107	13.0	(0)	9.05
D21B-1B	0.000103	13.8	(0)	9.50
D21B-1C	0.000098	14.0	(0)	9.75
D21B-2A	0.000114	13.0	(0)	9.00
D21B-2B	0.000102	13.5	(0)	9.20
D21B-2C	0.000095	14.2	(0)	9.85

nickel deposits prepared from the bath. The cathodic current density in each case was 40 amps per square foot. The thickness of the deposit was about 0.0001 inch.

Five deposit panels were prepared at temperatures in the range from 40 to 80°C at 10°C intervals. Three samples were taken from each panel and the permeability of these samples to helium gas was measured at one atmosphere overpressure. The permeability constants which were obtained from the measurements are listed in Table V.

When the log permeability constant is plotted as a function of the temperature of the plating bath, as in Figure 9, a straight line is obtained with a large positive slope. The permeability was found to increase exponentially with the temperature according to the empirical formula

$$\log k = 1.34\,T + \log A$$

$$k = A\,e^{1.34\,T} \quad \text{(where } A \text{ is a constant)}$$

Lyons (23) has shown how the coordination of water and organic molecules (in the case of the organic type bright baths) with the metal atoms on the crystal growing in the deposit explains the presence of both water and organic material in the deposit as found by chemical analysis. The coordinated water molecules eventually arrest the growth of the crystal in the Watts type deposit and remain on its surface in the grain boundary. Out-gassing the deposit into a high vacuum must remove water from the intergranular boundaries and leave a void for the passage of gas through the grain boundaries.

TABLE V

DATA SHOWING THE EFFECT OF TEMPERATURE OF THE PLATING BATH UPON THE PERMEABILITY

	Temperature of the Bath				
	40°C 104°F	50°C 122°F	60°C 140°F	70°C 158°F	80°C 176°F
$K_{He} \times 10^8$ (1./cm.^{2}min.)	1.75	3.35	6.20	11.5	21.5
	1.80	3.40	6.25	11.5	21.5
	1.80	3.35	6.30	12.0	21.5

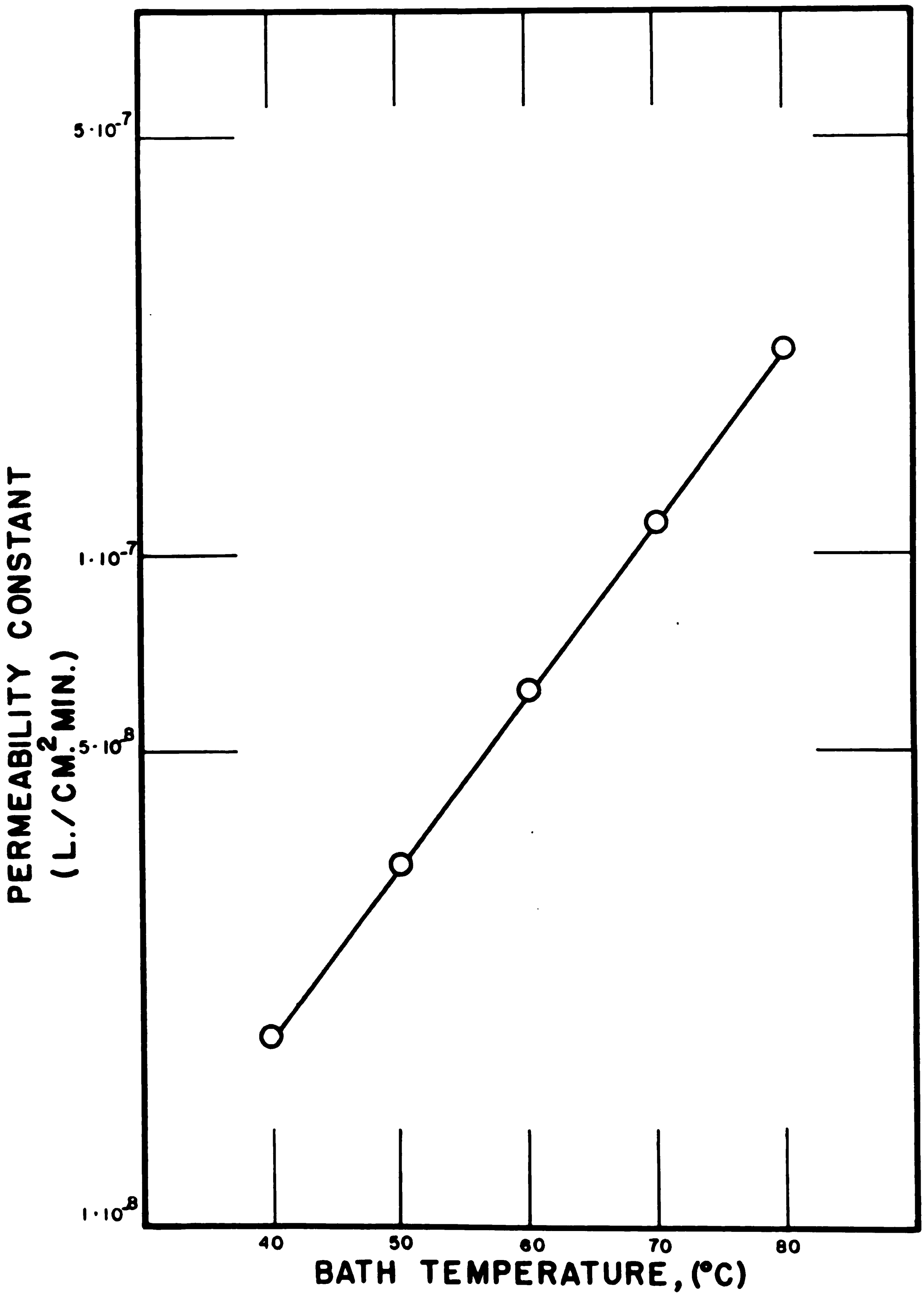

Figure 9. A graph showing the effect of temperature upon the permeability, on semi-log paper.

An interpretation which may be made for the increase in permeability with temperature of the bath is that the amount of water coordinated to the metal crystal surface increases with the temperature. The larger the amount of water in the grain boundary when the growth of the crystal is arrested, the larger the void in the grain boundary and the higher the permeability of the deposit to gases.

In support of this hypothesis, it was generally found that the higher the permeability of the deposit the longer time was required for out-gassing the deposit.

Cathodic Current Density

The usual current density used in the deposition of nickel is between 40 and 50 amps per square foot. Higher current densities would be desirable but the speed of deposition is limited by the process of diffusion of ions up to the cathode. The ionic mobilities can be increased somewhat by heating the bath if higher current densities are necessary. However, the most satisfactory deposits are obtained at a current density of 40 amps per square foot.

A Watts type bath at a pH of 2.2 was chosen for the study of the effect of the cathodic current density upon the permeability of the nickel deposited from the bath. The temperature of the bath was kept at 55°C.

Six deposit panels were prepared at values of cathodic current density in the range from 30 to 80 amps per square foot at 10 amps per square foot intervals. Three samples were taken from each panel and the permeability of these samples to helium gas was measured at one atmosphere of overpressure. The permeability constants which were obtained from the measurements are listed in Table VI. The thickness of all the samples was about 0.0001 inch.

The log permeability constant was plotted as a function of cathodic current density as shown in Figure 10. In general, the permeability of the deposit was found to increase with increasing current density, but the effect levels off at high current densities.

Nickel Salt Concentration in the Plating Bath

If the current efficiency is lower at the anode than at the cathode, nickel is removed from the bath at a faster rate than it is replenished by dissolution of the nickel anode. When this occurs, the nickel salt concentration falls in the bath. The nickel salts are also removed continually from the bath by another process called "dragout". This results from incomplete draining of the plating bath from the article when it is removed from the bath.

Commercial plating baths are operated for months or years, and the nickel salt concentration sometimes falls to a very low value before the salts are replenished. As the nickel salt concentration decreases, the current efficiency at both electrodes falls rapidly. At the cathode the current efficiency falls because of the codeposition of hydrogen. Of course, the lower the pH, the more hydrogen is codeposited.

A series of nine nickel plating baths were prepared in which the concentration of the nickel salts was decreased for each successive bath

TABLE VI

DATA SHOWING THE EFFECT OF CURRENT DENSITY UPON THE PERMEABILITY

	Current Density at the Cathode (Amps Per Square Foot)					
	30	40	50	60	70	80
$K_{He} \times 10^8$ (l./cm.^{2}min.)	3.70	6.30	8.65	10.5	11.5	12.0
	3.70	6.25	8.70	11.0	11.5	12.5
	3.75	6.25	8.60	10.5	11.5	12.0

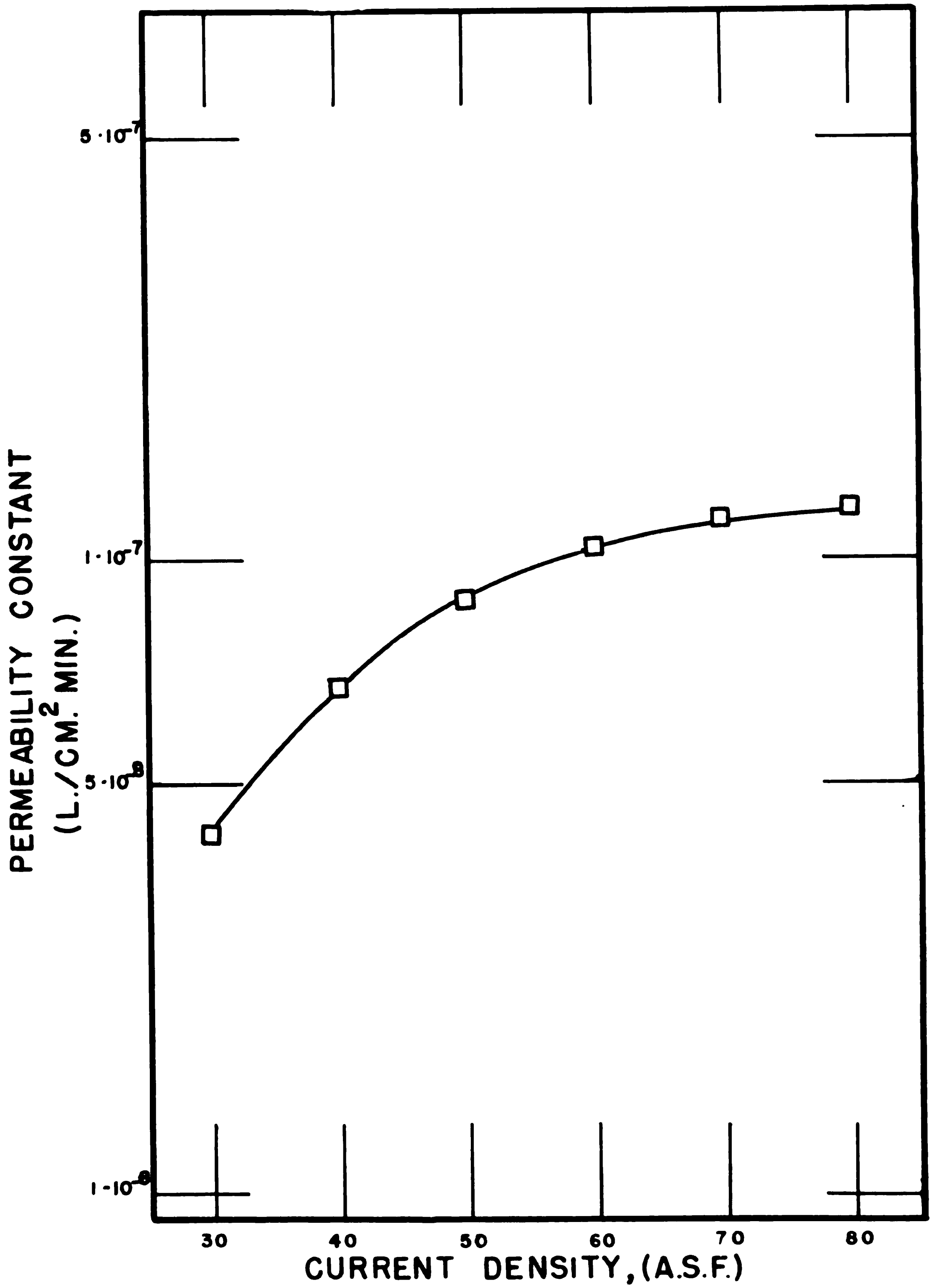

Figure 10. A graph showing the effect of cathodic current density upon the permeability plotted on semi-log paper.

by 10 per cent of the concentration which is normally used in a Watts type bath. In Table VII are listed the concentrations of nickel sulfate, nickel chloride and boric acid used in each bath. The boric acid concentration was kept at the concentration normally used in the Watts type bath. The ratio of the sulfate to chloride anions was also kept constant.

When deposit panels were prepared from the nine baths, the rate of deposition was found to decrease considerably at the lower nickel salt concentrations. Since the deposit samples were to be compared at the same thickness, 0.0001 inch, it was necessary to determine the rate of deposition in order to plate deposits of that thickness. The rate of deposition and the potential drop across the cell are recorded in Table VIII for each of the nine baths at three pH values, 2.2, 3.2, and 5.2.

One deposit panel was prepared from each of the nine baths at each pH value. Since three pH values were used, a total of twenty-seven deposit panels were prepared. The pH values were the same as those used in the study of the effect of pH on the permeability. The plating bath was kept at 55°C and the cathodic current density was 40 amps per square foot for each of the panels.

Although each of the baths was freshly purified and filtered, some of the baths developed a colloidal precipitate on electrolysis. The colloid was observed by the Tyndall effect using a strong light. This occurred only in the case of the plating baths at the higher pH of 5.2, and was most evident at about 50 per cent of the nickel salt concentration

TABLE VII

A LIST OF NINE BATHS WITH DECREASING NICKEL SALT CONCENTRATION

Percent of Normal Nickel Concentration	$NiSO_4 \cdot 6 H_2O$ (g./l.)	$NiCl_2 \cdot 6 H_2O$ (g./l.)	Boric Acid (g./l.)
100	240	45.0	30
90	216	40.5	30
80	192	36.0	30
70	168	31.5	30
60	144	27.0	30
50	120	22.5	30
40	96	18.0	30
30	72	13.5	30
20	48	9.0	30

TABLE VIII

DATA SHOWING THE EFFECT OF DECREASING NICKEL SALT CONCENTRATION UPON THE RATE OF DEPOSITION OF NICKEL

Percent Of Normal Nickel Concentration	pH	Potential Drop (volts)	Rate Of Deposition (mils/min.)
100	5.2	4.35	0.0226
	3.2	4.30	0.0225
	2.2	4.25	0.0206
90	5.2	4.40	0.0235
	3.2	4.35	0.0235
	2.2	4.30	0.0215
80	5.2	4.75	0.0243
	3.2	4.70	0.0241
	2.2	4.50	0.0225
70	5.2	5.10	0.0244
	3.2	5.05	0.0241
	2.2	4.85	0.0227
60	5.2	5.65	0.0241
	3.2	5.55	0.0238
	2.2	5.15	0.0223
50	5.2	6.3	0.0240
	3.2	6.2	0.0236
	2.2	6.1	0.0214
40	5.2	7.1	0.0239
	3.2	6.9	0.0235
	2.2	6.4	0.0204
30	5.2	8.9	0.0238
	3.2	8.5	0.0233
	2.2	7.9	0.0195
20	5.2	11.9	0.0236
	3.2	11.3	0.0210
	2.2	9.8	0.0187

Plating Conditions:
C.D. 40 a.s.f.
T 55°C(132°F)

normally used in the Watts type bath. On filtration through diatomaceous earth, the colloid was found to be green in color and probably was a basic nickel compound.

Three samples of each deposit panel were used for the measurement of the permeability of the nickel deposits to helium gas at one atmosphere overpressure. The permeability constants were calculated and are listed in Table IX.

When the log permeability constant is plotted as a function of the percent of normal nickel concentration on the basis of the Watts type bath being 100 per cent as shown in Figure 11, three interesting curves are obtained at the three pH values.

A large increase in permeability is observed in the case of the deposits from the series of plating baths at a pH of 5.2. As the nickel salt concentration decreases, the permeability rises quickly to a maximum at about 50 per cent of the normal nickel salt concentration and then decreases at still lower nickel concentrations. The maximum in the permeability occurs in those deposits produced from the baths which had developed a colloidal precipitate upon electrolysis. This was probably more than a coincidence since later investigations showed that the intentional addition of one part per million of three different colloids to a Watts type bath caused a thousandfold increase in the permeability.

A slight maximum in the curve for the series of baths at a pH of 3.2 was observed at about 80 per cent of the normal nickel salt concentration. No colloid was observed in the plating baths but a small

TABLE IX

DATA SHOWING THE EFFECT OF DECREASING NICKEL SALT CONCENTRATION UPON THE PERMEABILITY

Percent Of Normal Nickel Concentration	Permeability Constants, K_{He} (l./cm.^{2}min.) x 10^8		
	pH = 5.2	pH = 3.2	pH = 2.2
100	9.5	10.0	6.4
	9.6	10.5	6.5
	9.6	11.5	6.4
90	11.0	12.0	6.5
	11.5	12.0	6.6
	11.0	12.5	6.5
80	17.5	13.5	6.6
	17.0	13.0	6.6
	18.0	13.5	6.6
70	31.0	13.5	6.7
	32.0	13.0	6.6
	32.5	13.5	6.8
60	50.0	13.0	7.1
	52.5	13.0	7.0
	53.5	12.5	7.0
50	57.0	12.5	7.0
	62.5	12.5	6.9
	58.0	12.5	6.8
40	18.5	12.0	7.9
	18.0	12.0	7.3
	19.5	11.5	7.4
30	13.5	11.0	7.7
	13.5	10.5	7.7
	14.0	10.5	7.8
20	12.0	10.0	8.3
	12.0	10.5	8.4
	12.5	10.0	8.3

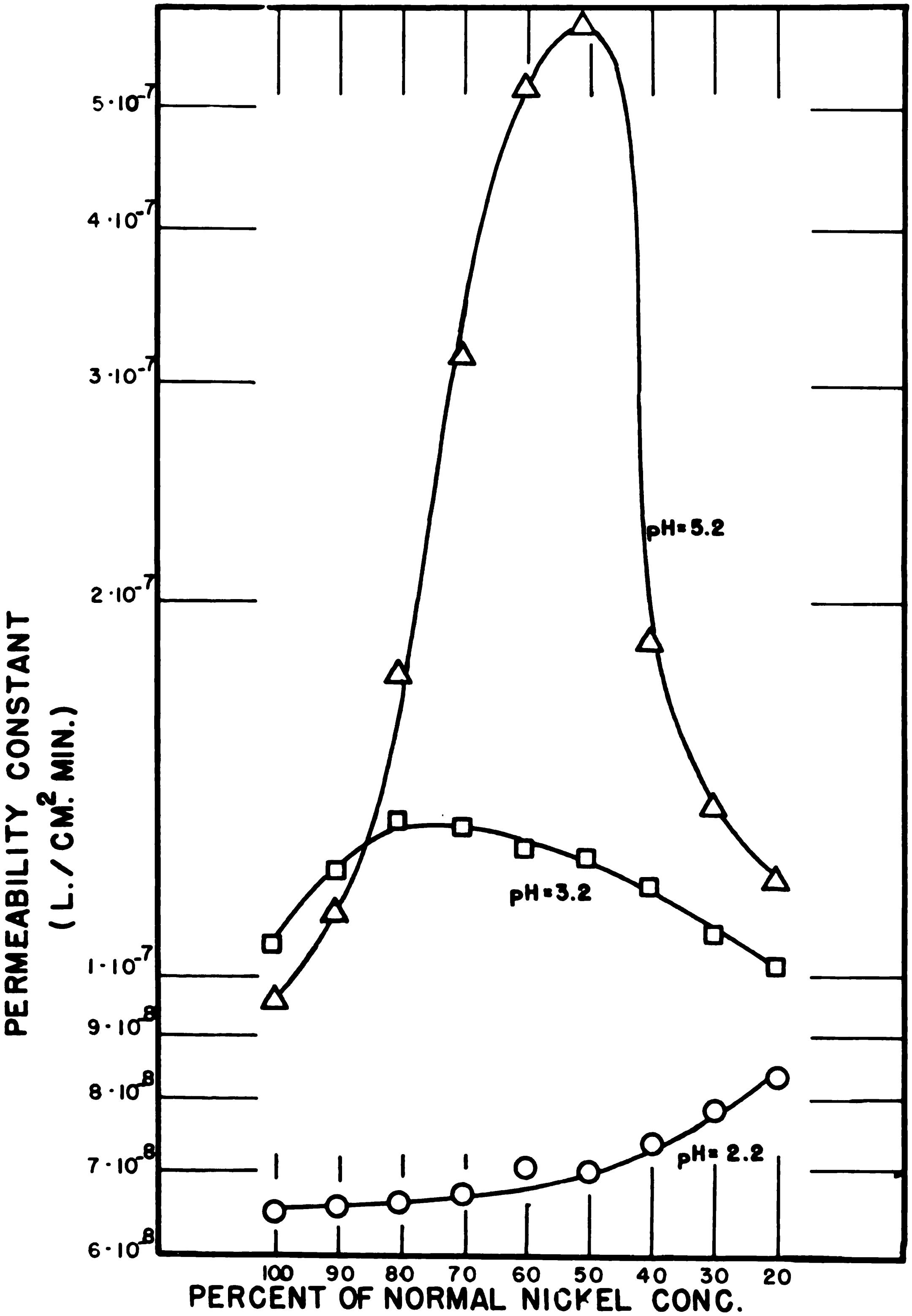

Figure 11. A graph showing the effect of decreasing nickel salt concentration upon the permeability plotted on semi-log paper.

amount may have been present in the layer immediately adjacent to the cathode.

In the case of the plating bath at a pH of 2.2, a steady but slight increase in permeability was observed. Some authors (24) have come to the conclusion that codeposition of hydrogen is the controlling factor in the porosity of electrodeposits. However, the intrinsic permeability of the deposits prepared from the series of baths at the lower pH of 2.2 increases only slightly while hydrogen is evolved profusely during deposition at the lower nickel concentrations.

Boric Acid Concentration in the Plating Bath

Boric acid is used in nickel plating because of its buffering action in the layer of plating bath adjacent to the xathode. When the plating bath becomes depleted in boric acid, the deposit changes from white to grey in color and the pH of the bath changes rapidly.

Boric acid is removed from the bath by "dragout" of plating solution on poorly drained articles removed from the bath, and by the deposition itself. Small quantities of boron can be detected spectrographically in the deposit.

Nine nickel plating baths were prepared in which the amount of boric acid was decreased by 10 per cent of the normal concentration used in the Watts bath for each bath. The composition of the nine baths is shown in Table X.

A decrease in the boric acid concentration does not materially affect the rate of deposition as was the case for decrease in nickel salt concentration.

TABLE X

A LIST OF NINE BATHS WITH DECREASING BORIC ACID CONCENTRATION

Percent of Normal Boric Acid Concentration	$NiSO_4 \cdot 6H_2O$ (g./l.)	$NiCl_2 \cdot 6H_2O$ (g./l.)	Boric Acid (g./l.)
100	240	45	30
90	240	45	27
80	240	45	24
70	240	45	21
60	240	45	18
50	240	45	15
40	240	45	12
30	240	45	9
20	240	45	6

The baths were operated at 55°C and the cathodic current density in each case was 40 amps per square foot. During deposition a colloid was seen to be formed in the bath in the case of the baths at a pH of 5.2 and low boric acid concentration.

One deposit panel was prepared from each of the nine baths at each of three pH values. Thus, twenty seven deposit panels were prepared. The pH values were 2.2, 3.2, and 5.2. The deposit samples were about 0.0001 inch thick.

Three samples of each deposit panel were used for the measurement of the permeability of the nickel deposits to helium gas at one atmosphere overpressure. The permeability constants were calculated and are listed in Table XI.

In Figure 12 are shown the curves obtained by plotting log permeability constant as a function of the per cent of the normal boric acid concentration used in the Watts type bath. The log permeability constant increases linearly in the case of the two lower pH values. However, the curve obtained for the bath at the pH value of 5.2 shows a very rapid increase in the permeability with decrease in boric acid concentration. This is probably caused by the colloid which was observed in those baths.

Bright Nickel Plating Baths

There are two types of bright nickel plating baths, the organic bright nickel plating and the alloy type bright nickel plating bath.

The organic type baths are usually very similar in composition to the Watts type bath, but always include two or three organic compounds

TABLE XI

DATA SHOWING THE EFFECT OF DECREASING BORIC ACID CONCENTRATION UPON THE PERMEABILITY

Percent of Normal Boric Acid Concentration	Permeability Constants, K_{He} (l./cm.^{2}min.) x 10^8		
	pH = 5.2	pH = 3.2	pH = 2.2
100	9.5	10.5	6.50
	9.0	11.0	6.30
	9.3	10.5	6.30
90	10.0	12.0	6.70
	10.0	12.0	6.50
	10.5	12.0	6.70
80	11.0	14.0	7.00
	11.5	13.5	7.00
	12.0	13.0	7.10
70	13.0	17.5	7.30
	13.0	14.0	7.40
	13.0	14.5	7.40
60	16.5	15.5	8.00
	16.0	15.5	7.90
	16.0	15.5	7.90
50	20.0	16.5	8.30
	21.0	17.0	8.10
	20.5	17.0	8.30
40	32.0	18.5	8.50
	32.0	19.0	8.60
	31.5	18.5	8.50
30	45.0	20.0	9.00
	46.0	20.5	9.00
	45.5	21.0	9.10
20	59.5	21.5	9.45
	60.5	21.5	9.50
	60.0	22.0	9.50

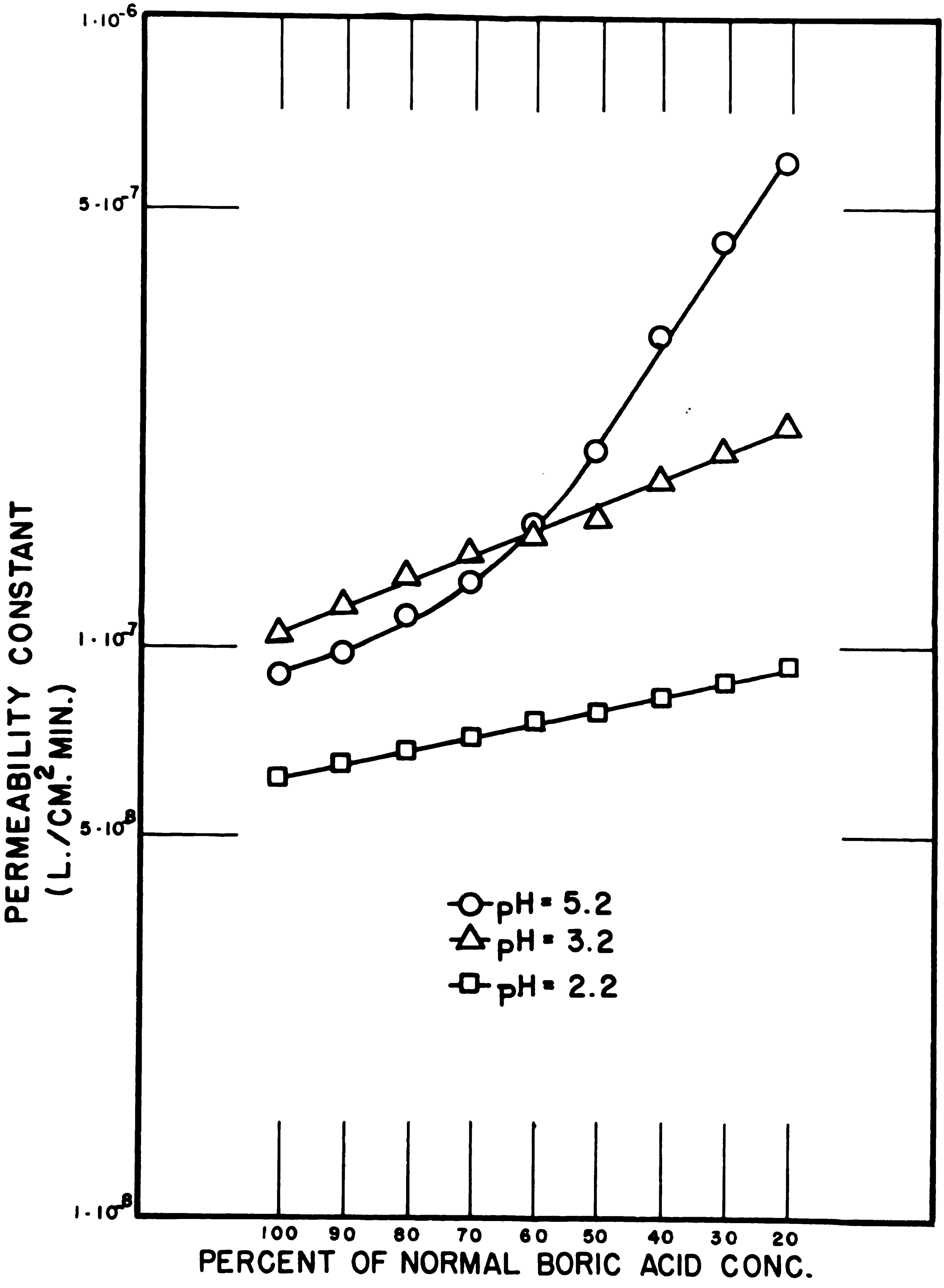

Figure 12. A graph showing the effect of decreasing boric acid concentration upon the permeability plotted on semi-log paper.

added for their effect in producing a bright deposit. The commercial baths generally have a polysulfonated benzene or napthalene for a primary brightener, but they differ widely in the secondary brightener which is used. A third organic addition agent common to the baths is some surface active agent used for the purpose of decreasing the surface tension of the bath, such as a sodium alkyl sulfonate. The latter compounds are called anti-pitters, because they tend to release the hydrogen bubbles which become attached to the deposit. Six bright nickel deposits from commercial plating baths were measured to find if there were significant differences in the permeability resulting from the addition of the organic compounds to the Watts type bath.

The other type of bright nickel bath is the alloy type, which is less commonly used. It is considerably different from the Watts type bath. Formic acid is used instead of boric acid as a buffer. Formaldehyde is used as an anti-pitter and some of the nickel salt is replaced by the corresponding cobalt salt. These are the main differences. One example of the nickel-cobalt bright deposit was studied for comparison with the organic type bright nickel deposits.

The sulfamate nickel bath is not a bright nickel bath, but it was studied because of its close similarity to the Watts type bath in composition and in the way it responds to the addition of trisulfonated napthalene. In composition it differs from the Watts type bath in one significant respect, that nickel sulfamate is used instead of nickel sulfate. Sulfamic acid may be thought of as sulfuric acid with one of the hydroxyl groups replaced by an amino group.

Table XII lists the various types of baths which were studied and the letter which was used to designate the particular baths. The optimum bath temperature, pH and cathodic current density suggested by the company supplying each bath are also listed in the table.

Each of the baths was purified in the manner described by the supplier. The deposits from all the bright baths were quite bright, smooth and white in color. A deposit panel was prepared from each of the above baths using the plating conditions given in Table XII. The thickness of each deposit panel was about 0.0001 inch.

The permeability of six samples taken from each panel to hydrogen and helium gases at one atmosphere of overpressure was measured. The permeability constants were calculated from the rates of flow and the values for the six samples from any one panel were averaged. The mean value is listed in Table XIII, along with the values already obtained for the Watts type deposit for the sake of comparison.

The deposits from the six organic type bright nickel baths (E,F,H,J,K,L) are less than one-half as permeable as the deposit from a Watts type bath at about the same pH value. Specimens of the bright deposit from bath (F) and the dull deposit from the Watts type bath (C) were examined at 1200 power magnification after polishing and etching. The cross-section of the bright deposit showed the typical laminar or striated structure usually found in the thicker deposits. The deposit from the Watts type bath clearly showed a granular structure. The larger grains extended from one surface of the deposit to the other, with smaller grains packed between them at the surface which was adjacent

TABLE XII

AN INDEX OF THE BATH SYMBOLS SHOWING THE BATH DESIGNATED BY EACH SYMBOL USED

Bath Symbol	Bath Type	Plating Conditions
A	Watts	pH 5.2, 60°C, 40 a.s.f.
B	Watts	pH 2.2, 60°C, 40 a.s.f.
C	Watts	pH 3.2, 55°C, 40 a.s.f.
D	Watts	pH 5.2, 55°C, 40 a.s.f.
E	Organic Bright	pH 3.2, 55°C, 40 a.s.f.
F	Organic Bright	pH 3.5, 50°C, 40 a.s.f.
G	Watts	pH 2.2, 55°C, 40 a.s.f.
H	Organic Bright	pH 3.5, 50°C, 40 a.s.f.
I	Nickel Cobalt-9H	pH 3.7, 55°C, 40 a.s.f.
J	Organic Bright	pH 3.2, 55°C, 40 a.s.f.
K	Organic Bright	pH 3.5, 60°C, 40 a.s.f.
L	Organic Bright	pH 3.7, 55°C, 40 a.s.f.
M	Nickel Sulfamate	pH 3.5, 50°C, 40 a.s.f.
N	Nickel Sulfamate Plus Brightener	pH 3.5, 50°C, 40 a.s.f.

TABLE XIII

A LIST OF PERMEABILITY CONSTANTS FOR THE BATHS GIVEN IN THE INDEX

Bath Symbol	Permeability Constants, (l./cm.^{2}min.)		
	$K_{H_2} \times 10^8$	K_{N_2}	$K_{He} \times 10^8$
C	14.5	(0)	10.5
D	13.8	(0)	9.65
E	4.65	(0)	3.30
F	3.63	(0)	2.60
G	9.15	(0)	6.40
H	4.85	(0)	3.35
I	9.20	(0)	6.45
J	3.40	(0)	2.35
K	4.35	(0)	2.95
L	3.80	(0)	2.60
M	9.95	(0)	7.15
N	7.65	(0)	5.40

Note: Each value in the above table is a mean of six values obtained experimentally. The deviation is less than five percent.

to the base metal. The laminar structure is apparently less permeable to gases than the granular structure of the Watts bath deposit.

The permeability of the bright deposit from the nickel-cobalt bath (I) was found to be slightly less permeable than the Watts type bath (C) deposit.

The deposit obtained from the nickel sulfamate bath (M) was slightly less permeable to gases than the deposit from the Watts type bath (C). When 7.5 grams per liter of napthalene-1,3,6-trisulfonic acid was added to the bath to prepare bath (N), the nickel deposit was much brighter and the permeability to gases was found to decrease.

Colloidal Impurities in the Plating Bath

Several colloidal impurities are often found in nickel plating baths. For the successful operation of any nickel plating bath, batchwise filtration of the bath is necessary and continuous filtration is advisable.

As the nickel anode dissolves, the carbon present in the cast metal is freed and forms a black anode slime. In order to prevent the anode slime from dispersing in the plating bath, the anodes are always placed in cloth anode bags.

Sometimes the sizing of the material used in a new anode bag will get into the plating bath. Starches and gums can have a very pronounced deleterious effect upon the appearance of a nickel deposit.

Other colloidal material which may enter a plating bath are the dust and dirt which settle from the air and basic nickel compounds precipitating from the bath at higher pH values.

Three Watts type baths were prepared for the study of the effect of colloidal impurities upon the permeability of nickel deposits to gases. One part per million of gelatin was dissolved in the first bath. One part per million of colloidal graphite (Aquadag) was dispersed in the second bath by slowly adding the nickel bath to the graphite suspension and stirring. One part per million of black anode slime was dispersed in the third bath. The pH of the baths was 2.2, the temperature was 55°C and the cathodic current density was 40 amps per square foot.

Three deposit panels were prepared of about 0.0001 inch thickness. Three samples were taken from each panel and were tested as usual to determine the presence of photographable pores. Since no photographable pores were found, the permeability of the deposit samples to helium gas at one atmosphere overpressure was measured. The permeability constants were calculated and are listed in Table XIV.

The addition of all three colloids caused a very marked increase in the permeability of the nickel deposits to gases. The increase was about a thousandfold.

Metallic Impurities in the Plating Bath

Metallic impurities are very common in plating baths because of the numerous ways in which they can be introduced into the bath. The impurities may be present in the water used to maintain the bath at a constant volume. They may come from corrosion products of metal bus bars and other fixtures over the plating tank. An article may fall

TABLE XIV

DATA SHOWING THE EFFECT OF THE ADDITION OF COLLOIDAL IMPURITIES TO THE BATH UPON THE PERMEABILITY

Impurity	Amount	Permeability Constants, K_{He} (l./cm.^{2}min.) x 10^8		
Gelatin	1.0 p.p.m.	6,000	7,000	7,000
Colloidal Graphite	1.0 p.p.m.	9,000	10,000	30,000
Anode Slime	1.0 p.p.m.	20,000	40,000	20,000

off the plating rack and dissolve slowly at the bottom of the tank. Chromium and copper plating baths in neighboring plating tanks are dispersed into air-borne droplets at the electrodes and may find their way into the nickel plating bath.

Three very common and troublesome impurities are iron, copper and zinc. Three Watts type baths were prepared and five parts per million of these impurities was introduced into separate baths in the form of the sulfate. Ferric sulfate was added to the first bath, copper sulfate to the second and zinc sulfate to the third. After a deposit panel was prepared from each of the impure baths, the amount of impurity in the baths was increased to ten parts per million. Then, three more deposit panels were prepared. The deposits were dark in appearance, particularly the two panels obtained from the bath containing copper as an impurity.

The pH of the baths was adjusted to 2.2. The temperature of the baths was 55°C and the cathodic current density was 40 amps per square foot. The thickness of the deposit panels was about 0.0001 inch.

Three samples were taken from each of the six deposit panels. The permeability of the deposit samples was measured using helium gas at one atmosphere of overpressure. The permeability constants which were obtained are listed in Table XV.

A very definite increase in permeability is noted in all the deposits, as is shown in Figure 13. Copper is seen to have a greater effect than the same amount of iron or zinc. It is also the most troublesome metallic impurity in a nickel plating bath.

TABLE XV

DATA SHOWING THE EFFECT OF THE ADDITION OF METALLIC IMPURITIES TO THE BATH UPON THE PERMEABILITY

Amount (p.p.m.)	Impurity					
	Fe(III) 5	Fe(III) 10	Cu(II) 5	Cu(II) 10	Zn(II) 5	Zn(II) 10
$K_{He} \times 10^8$ (l./cm.^{2}min.)	1.70	65.0	32.5	460	11.0	36.5
	1.20	65.5	33.0	475	11.0	37.0
	1.15	64.0	33.5	460	12.0	37.5

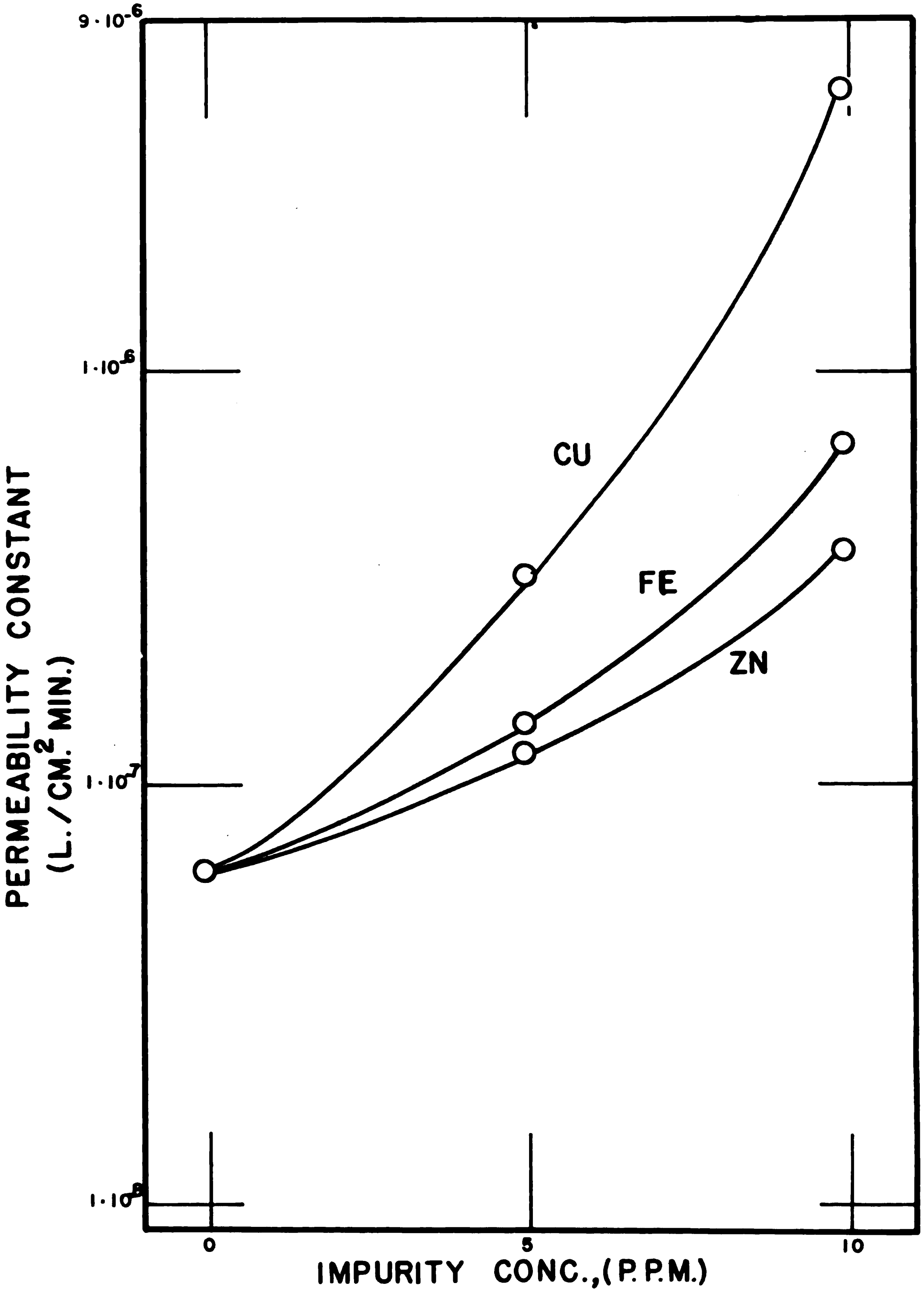

Figure 13. A graph showing the effect of the addition of several metallic impurities to the plating bath upon the permeability plotted on semi-log paper.

Base Metal Panel

Another base metal which might have been used for this investigation is stainless steel, the base metal used by Thon and by Ogburn. Nickel deposits are easily detached from stainless steel.

A comparison was made of the permeability of a nickel deposit prepared upon buffed nickel with a deposit prepared upon buffed stainless steel (18-8) in order to determine if the chemical nature of the base metal is important to the permeability.

The same bath was used for the preparation of both deposit panels. The Watts type bath was operated at a pH of 2.2, a temperature of 60°C and a cathodic current density of 40 amps per square foot.

Measurements of the permeability of six samples taken from each of the deposits to hydrogen and helium gases at one atmosphere of overpressure showed the deposits to have nearly identical permeabilities. The permeability constants are listed in Table XVI.

Both the nickel and the stainless steel panels were carefully buffed before the deposits were prepared, so they both had the disoriented surface of the Beilby layer (25). The lack of an oriented structure in both surfaces is probably responsible for the identical permeabilities of the deposits.

TABLE XVI

DATA SHOWING THE EFFECT OF USING TWO DIFFERENT METALS FOR THE BASE METAL UPON THE PERMEABILITY

Deposit Sample	Mean Thickness (in.)	$K_{H_2} \times 10^8$ (l./cm.^{2}min.)	K_{N_2}	$K_{He} \times 10^8$ (l./cm.^{2}min.)
		Stainless Steel Base		
B30B-1A	0.00015	8.6	(0)	6.0
B30B-1B	0.00013	8.8	(0)	6.2
B30B-1C	0.00011	9.3	(0)	6.5
B30B-2A	0.00013	8.8	(0)	6.2
B30B-2B	0.00012	8.8	(0)	6.2
B30B-2C	0.00010	9.2	(0)	6.1
		Buffed Nickel Base		
B19A-1A	0.000093	8.7	(0)	6.1
B19A-1B	0.000098	9.0	(0)	6.3
B19A-1C	0.000104	9.2	(0)	6.5
B19A-2A	0.000087	8.5	(0)	5.9
B19A-2B	0.000101	8.9	(0)	6.5
B19A-2C	0.000108	9.4	(0)	6.7

V. SUMMARY AND CONCLUSIONS

Summary

Thin, detached nickel electrodeposits have been found to be much more permeable to gases than nickel foils produced by casting and hot rolling. The difference in permeability has been shown to be caused by the presence of grain boundary diffusion through the voids between the crystal grains in the electrodeposited metal. Helium diffuses through detached nickel deposit but not through rolled nickel because it is not soluble in nickel nor will it diffuse interstitially through the crystal lattice.

The permeability of nickel deposited from a Watts type bath was found to decrease with the thickness at a greater rate than would be expected from the simple proportionality of permeability to reciprocal thickness. This was related to the change in the character of the microstructure of the deposit with increasing thickness.

The pH of a Watts type bath was found to have little effect upon the permeability of the deposit. However, the permeability increased with increases in both the bath temperature and the cathodic current density.

Increases in permeability were obtained by independently decreasing the nickel salt and the boric acid concentrations in the plating bath. The increases in permeability were much greater in the case of the baths at a pH of 5.2 than at the lower pH values. This was probably caused by the formation of a colloid in the plating bath during deposition at the higher pH.

Bright nickel deposits from the organic type bright nickel baths were found to be less than half as permeable as the deposits from a Watts type bath at about the same pH. This may be caused by the laminar structure of the bright deposit breaking up the grain boundary pattern and making a more tortuous route for the permeation of gases. Metallographic studies of the organic bright nickel deposit showed the laminar structure while the Watts type deposit exhibited large grains extending from the one surface of the deposit to the other.

Deposits prepared from the nickel-cobalt bright bath and the nickel sulfamate bath were found to be only slightly less permeable to gases than the Watts type deposit. Addition of the primary brightener napthalene tri-1,3,6-trisulfonic acid to the nickel sulfamate bath changed the dull deposit to semi-bright and decreased the permeability of the deposit to gases.

The use of stainless steel as a base metal had no effect upon the permeability of the nickel deposits. Buffed nickel was chosen for the base metal only because it was easier to buff than the stainless steel.

An estimation of the precision involved in the determination of the permeability constant indicates the degree of reproducibility of the results obtained in this investigation. There is not sufficient data to warrant a mathematical analysis of the error, so the residuals for two series of measurements were calculated. The residual is often called the error and is defined as the difference between a particular measurement and the mean value of the series of measurements, which is assumed to be the true value of the measurement. If the residuals are small compared with the magnitude of the measurement, the measurement is said to be precise. In physical chemistry the most common procedure is to give the average error, which is defined in terms of the residual, r, and the number of measurements, n, as follows:

$$\text{Average error} = \pm \frac{\Sigma(r)}{n}$$

The permeability constant for a nickel deposit prepared from a Watts type bath at a pH of 2.2, a cathodic current density of 40 amps per square foot and a temperature of 55°C has been measured fifteen times. The permeability constant with its average error is:

$$k_{He} \ (\text{l./cm.}^2\text{min.}) \times 10^8 = 6.29 \pm 0.11$$

The value for the permeability constant which can be obtained for the bath at 55°C by interpolation from the log permeability constant versus bath temperature curve is 28 per cent lower than the mean value. There is probably an unrecognized source of systematic error in that particular curve. However, the actually measured values on the curve for the bath at 60°C are in much better agreement, but are still on the low side of the mean value for the constant at that temperature.

In general, the residuals of actually measured values deviate from the mean value by less than five per cent.

Conclusions

The most important variable of the ones which were studied was the effect of the addition of metallic and colloidal impurities to the bath. Ten parts per million of copper, iron and zinc sulfates were added to Watts type nickel baths and the deposits from the baths were found to have permeabilities ten to a hundred times greater than that of deposits from the pure Watts bath. Copper was found to give the greatest increase in permeability.

One part per million of gelatin, colloidal graphite and black anode slime were added to Watts type nickel baths. The effect upon the permeability was even greater than in the case of the metallic impurities. The permeabilities were found to have increased a thousand fold, and yet the deposits appeared to be the same as the deposits from the pure Watts type bath.

In conclusion it should be mentioned that the intrinsic permeability has not been definitely related to the corrosion protection afforded by the nickel deposit in this investigation, but work has been begun by the author for that purpose. It has already been shown by both Thon (11) and Fay (15) that the permeability to gases does increase rapidly upon exposure of the nickel deposit to several corrosive environments.

Gas pores and deposit faults over pits, scratches and inclusions in the base metal may be more important in limiting the service life of a plated article, however, it has been clearly shown by this investigation that the most important variable leading to high deposit permeability is the presence of metallic and colloidal impurities in the bath.

LITERATURE CITED

1. Thon, N., and Addison, E. T., Monthly Rev. Am. Electroplaters Soc., 34, 568-76, 722-30 (1947).

2. Blum, W., and Hogaboom, G. M., "Principles of Electroplating and Electroforming," McGraw-Hill Book Company, New York, 1930, p. 125.

3. Thon, N., and Addison, E. T., Monthly Rev. Am. Electroplaters Soc., 34, 831-42 (1947).

4. Blum, W., and Hogaboom, G. M., "Principles of Electroplating and Electroforming," McGraw-Hill Book Company, New York, 1930, pp. 132-3, 136-7.

5. Thon, N., and Addison, E. T., Monthly Rev. Am. Electroplaters Soc., 34, 445-53 (1947).

6. Thon, N., and Kelemen, D., Plating, 35, 917-20, 967 (1948).

7. Thon, N., et al., Plating, 36, 362-6 (1949).

8. Thon, N., and Dean, D., Plating, 41, 503-5 (1954).

9. Thon, N., et al., Plating, 37, 631-2 (1950).

10. Thon, N., et al., Plating, 37, 280-4 (1950).

11. Thon, N., et al., Plating, 36, 928-9 (1949).

12. Thon, N., et al., Plating, 40, 1011-5 (1953).

13. Thon, N., et al., Plating, 40, 1135-7 (1953).

14. Ogburn, F., and Benderly, A., Plating, 41, 61-5, 169-73 (1954).

15. Fay, R., Ph. D. Thesis, Michigan State College, 1954.

16. Ewing, D. T., et al., Plating, 36, 1137-45 (1949).

17. Metal Finishing Guidebook and Directory, 1950, p. 449.

18. Barrer, R. M., "Diffusion In and Through Solids," Cambridge Press at the University, Cambridge, 1951, p. 70.

19. Brenner, A., <u>et</u> <u>al</u>., Plating, <u>39</u>, 865-926 (1952).

20. Barrer, R. M., "Diffusion In and Through Solids," Cambridge Press at the University, Cambridge, 1951, pp. 144-205.

21. Barrer, R. M., "Diffusion In and Through Solids," Cambridge Press at the University, Cambridge, 1951, p. 207.

22. Barrerm R. M., "Diffusion In and Through Solids," Cambridge Press at the University, Cambridge, 1951, pp. 53-5.

23. Lyons, E. H. Jr., J. Electrochem. Soc., <u>101</u>, 376-81 (1954).

24. Blum, W., and Hogaboom, G. M., "Principles of Electroplating and Electroforming," McGraw-Hill Book Company, New York, 1930, pp. 110, 240, 266.

25. Adam, N. K., "The Physics and Chemistry of Surfaces," Oxford University Press, London, 1949 (third edition), pp. 170-4.