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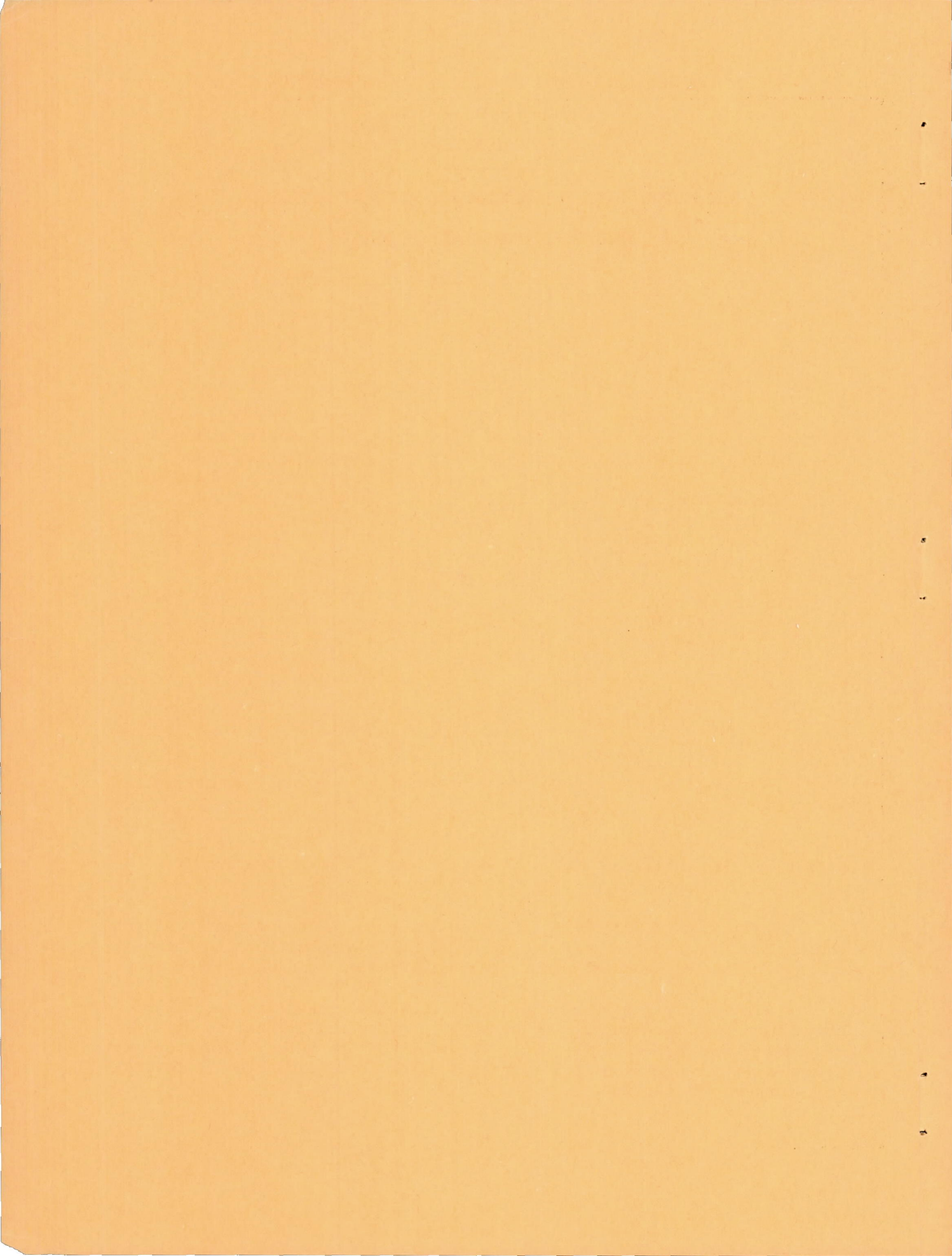# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3577

THE NICKEL DIP: A RADIOISOTOPE STUDY OF METALLIC

DEPOSITS IN PORCELAIN ENAMELING

By Joseph C. Richmond, Harry B. Kirkpatrick,
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National Bureau of Standards

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SUMMARY

Radioisotope tracer techniques were used to study the following
phenomena: (1) The effect of the nickel dip on the deposition of cobalt
metal during firing of a cobalt-bearing ground coat on pickled and sand-
blasted iron, (2) the effect of surface pretreatment on the amount and
distribution of nickel deposited from the nickel dip on enameling iron,
and (3) the effect of application and firing of cobalt-free and cobalt-
bearing enamels on the chemical form and physical distribution of nickel
previously deposited on enameling iron by the nickel dip.

The use of radioactive nickel in the nickel-dip solution was found
to offer several advantages for studying the deposition of nickel by this
process. Autoradiographs give an informative picture of the actual dis-
tribution of the deposit with good resolution. Radioassays are a quick,
nondestructive method of determining the amount of nickel deposited, and
radioassays were made on the same area of specimens at various stages in
the processing to evaluate the effect of various treatments on the amount
of nickel retained by the iron.

The results of the several experiments may be briefly summarized
as follows:

(1) The presence of nickel from the nickel dip had little or no
effect on the deposition of cobalt metal during firing of a cobalt-
bearing enamel on iron.

(2) The type of cleaning (sandblasting or pickling) markedly affected
the amount of cobalt deposited during firing of a cobalt-bearing enamel
on iron. Heavier deposits occurred on sandblasted than on pickled iron.

(3) The distribution of the nickel from the nickel dip was always
nonuniform, but the size of the areas of heavier and lighter deposits
was markedly affected by the prior treatment of the metal. Heavy deposits
occurred at scratches and other areas that had been subjected to severe
cold-work in the surface.

(4) The nickel from the nickel dip remained as metal at the enamel-metal interface during firing of both cobalt-bearing and cobalt-free enamels on nickel-dipped iron. There was no evidence of oxidation of the nickel followed by solution into the enamel glass, but there was some evidence that part of the nickel was separated from the metal upon continued firing, probably by undercutting.

INTRODUCTION

The mechanism responsible for the bonding of ceramics to metals has been under study for several years in the Enameled Metals Section of the National Bureau of Standards. Earlier reports (refs. 1, 2, and 3) were concerned with the manner in which adherence develops when cobalt ions are present in the coating. The first report (ref. 1), in which radio-active cobalt 60 was used as a tracer, demonstrated conclusively that cobalt metal plates onto the steel base during normal firing of a cobalt-bearing ground coat. Because of the success of this earlier tracer study, it was believed that similar techniques might be useful in a study of the nickel dip.

The nickel-dip treatment consists of immersing a freshly cleaned steel[1] sheet in an aqueous solution of a nickel salt. The nickel ions from solution, being more noble than the iron, are galvanically deposited on the steel as metal, while an equivalent amount of iron goes into solution. In practice, the concentration of nickel, the temperature and pH of the bath, and the time of immersion are closely controlled. The small deposit of nickel produced by this treatment, on the order of 70 milligrams per square foot, produces several beneficial effects during the subsequent enameling of the steel sheet, one of the most important of which is an improvement in adherence of the enamel to the steel.

The use of radioactive nickel in the nickel dip offers many advantages in studying the deposition that occurs during this process. Autoradiography gives an informative picture of the actual distribution of the deposit with good resolution. Radioassays offer a quick method of determining the amount of nickel deposited, which, because it is non-destructive, can be used at successive steps of processing on the same area of one specimen.

The present paper describes experiments in which radioisotope techniques were used to study: (1) The effect of the nickel dip on the deposition of cobalt metal during firing of a cobalt-bearing ground coat on pickled and sandblasted iron, (2) the effect of surface pretreatment on the amount and distribution of nickel deposited from the nickel dip on enameling iron, and (3) the effect of application and firing of cobalt-bearing and cobalt-free porcelain enamels on the chemical form and physical

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[1]The steel most commonly used for porcelain enameling is a low-carbon (0.05 percent or less), high-purity steel known to the trade as enameling iron.

distribution of the deposit from the nickel dip. A companion paper
(ref. 4) is concerned with evaluation of the effect of the nickel dip on
adherence and presents a theory to explain the bonding mechanism. This
study is one phase of a broader investigation of the adherence of ceramic
coatings to metals being conducted at the National Bureau of Standards
under the sponsorship and with the financial assistance of the National
Advisory Committee for Aeronautics.

MATERIALS AND GENERAL PROCEDURE

The radioactive isotopes used in this study were procured from the
Oak Ridge National Laboratory, Oak Ridge, Tenn. Radioactive cobalt 60
was used in the form of oxide produced by pile irradiation of normal
cobalt oxide which was chemically pure. This isotope is the same as
that used in a previous study (refs. 1 and 2). The radioactive nickel
63 was produced by pile irradiation of highly purified cobalt-free
nickel. It was converted to nickel ammonium sulfate at the Oak Ridge
National Laboratory before shipment.

Each of these isotopes can be positively identified when present
in microgram quantities provided there is no other radioactive constit-
uent of the sample; and, if the geometry, backscattering, and self-
absorption factors are known, quantitative determinations can be made.
The radioassay is rapid, usually requiring but 1 minute to obtain results
of satisfactory accuracy, and leaves the specimen unaffected by the
determination. The usual chemical analysis for nickel deposits on steel
requires that an area of 0.01 square foot be stripped to provide the
sample. This area is covered by a circle approximately $1\frac{3}{8}$ inches in
diameter. With radioactive nickel at the concentrations used in this
study, accurate radioassays could be made on an area as small an 1/8 inch
in diameter. The ratio of areas is about 120:1.

The use of autoradiography, in which a photographic film is placed
in contact with the specimen and is sensitized by particles emitted from
the radioactive isotope, offers a still higher degree of resolution,
which under the most favorable conditions may distinguish between areas
0.001 inch or less in diameter and 0.001 inch apart. The area involved
in this case is only about 1/1,800,000 as much as that normally used for
chemical analysis. In studying the distribution of thin deposits, there-
fore, the use of radioactive isotopes has great advantages. The amount
of darkening produced on a photographic film that has been exposed in
contact with a specimen containing a radioactive isotope deposited on
its surface will bear a direct relationship to the amount of the radio-
active isotope on the specimen. Also, the variation in the amount of dark-
ening, or the distribution of light and dark areas, will give a good picture
of the distribution of the deposit. Spurious effects can be produced, how-
ever, by self-absorption and reflection of the radiations, particularly if

the radioactive isotope is distributed within the body of the specimen. If the radioactive isotope is deposited on the surface of a specimen of uniform density, as in these experiments, spurious effects due to the surface texture of the specimen or to self-absorption of radiation within the deposited radioactive material can sometimes arise.

Ilford NTB film was used in making the autoradiographs of the metallographic sections and Eastman Super XX, for those of the large pickled specimens, the film being clamped against the specimen to insure contact.

Enameling grade of steel was used in all of the experiments reported in this paper and was of 20-gage thickness unless otherwise indicated. All specimens were cut to size, marked for identification, and punched for hanging before cleaning.

All pickling was done by the procedure outlined in table I, except that in some cases the nickel-dip treatment was omitted, in which cases steps 6 and 7 were bypassed, the specimens being transferred directly from the acid rinse, step 5, to the neutralizer, step 8. All sandblasting was done with 40-mesh glass sand, using 80 pounds of air pressure. Sandblasted specimens that were nickel dipped were treated as indicated in table I, beginning with step 6 and following through the remainder of the procedure.

The nickel-dip solution was prepared as indicated in table I, and to 1 liter of this solution was added 1 gram of the radioactive nickel ammonium sulfate $NiSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$ for those experiments in which radioactive nickel solution was used. This material had a specific activity of approximately 0.8 millicurie per gram.

Three ground-coat enamels were used: (1) A typical one-frit ground coat I-2 (ref. 1), (2) enamel I-2R, produced by addition of 0.0075 percent of radioactive cobalt 60 as oxide to the frit batch of enamel I-2 (ref. 1), and (3) enamel I-1, produced by elimination of the oxides of cobalt, nickel, and manganese from the frit of enamel I-2 (ref. 2). All enamels were prepared by standard procedures as outlined in reference 1 and were applied by dipping to produce an enamel of fired thickness of 0.005 ± 0.001 inch. The specimens were dried at 220° F and fired in an electrically heated box type of furnace under the conditions indicated in the tables.

Radioassays were made by counting the pulses produced by the action of the beta or gamma rays on a Geiger-Müller tube, the counts being indicated on a decade scaler. For the counts on metal specimens, a Tracerlab TGC-3 tube was used with no shielding. An aluminum cap with a 1-inch-diameter hole in the center was placed over the end of the tube, and this cap was held in close contact with the surface of a specimen during the count. For counts on chips or dried residues from solutions,

a Tracerlab TGC-1 tube, mounted inside a shield having lead walls 2 inches
thick, was used. In this case a plastic rack with adjustable shelves was
used to insure reproducible positioning of the specimens with respect to
the tube. The counts were corrected for background, but no corrections
were made for decay of the isotopes because the duration of the experiments
was negligible compared with the half lives.

A calibration experiment was performed to relate the radioassay counts
to the amount of nickel present on the specimens as determined by chemical
analysis. Ten 20-gage enameling-iron specimens 4 by 4 inches were pre-
pared. Five specimens were cleaned by pickling and five, by sandblasting.
These specimens were then treated in the radioactive nickel-dip solution
for various times to deposit different weights of nickel. A radioassay
was made on two marked areas on each specimen, and the count was recorded.
The amount of nickel on these areas was determined chemically by standard
colorimetric procedures, using the stripping method developed by Ikenberry
and Canfield (ref. 5).[2] The data are shown in figure 1 and indicate
excellent correlation between the radioassays and chemical determinations
of the nickel on the specimens treated with radioactive nickel. The fact
that the observed points fall along a straight line passing through the
origin indicates that spurious effects due to self-absorption of the
radioactive nickel were absent over the range of deposits covered in this
study.

<div align="center">EXPERIMENTAL PROCEDURE AND RESULTS</div>

Effect of nickel dip on cobalt deposition.- Twelve specimens,
2 by 4 inches in size, were prepared and marked for identification. Six
specimens, identified with the letter P, were cleaned by pickling; three,
Pl, P2, and P3, with the nonradioactive nickel dip; and three, P4, P5,
and P6, without. Six other specimens, identified with the letter S, were
cleaned by sandblasting, and three of them, S1, S2, and S3, were also
nickel dipped.

Radioactive cobalt-bearing enamel I-2R was applied to all specimens
and fired as indicated in table II. The specimens were then deenameled
in molten sodium hydroxide at about 800° F, allowed to cool in air,
rinsed in running hot water, and dried. Previous experiments (ref. 1)
have shown that this treatment removes the enamel layer and with it the
radioactive cobalt present as oxide. Counts were then made to compare
the amounts of metallic cobalt deposited on the steel from the enamel
during firing, under the various conditions.

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[2]The nickel determinations were made by Miss Nancy Balint, formerly
a member of the Enameled Metals Section.

The results, shown in table II, indicate that the nickel-dip treatment had little effect on the amount of cobalt metal deposited at the enamel-metal interface. Significant differences were found in the amounts of cobalt deposited on sandblasted and on pickled steel. In every case more cobalt was deposited on sandblasted than on pickled steel. The differences are greatest on the underfired specimens and decrease with increased firing.

Effect of cleaning treatment on deposition of nickel.- Several experiments were carried out to determine the effect of cleaning treatment on the amount and distribution of the nickel deposited from the nickel dip.

In order to make a preliminary test for spurious effects or anomalies due to the surface texture of the specimens, four specimens of 16-gage steel were treated to give surfaces of different degrees of roughness. One specimen was mechanically polished, one was pickled, one was sandblasted, and one was sandblasted and then pickled. Each of the specimens was then plated with radioactive nickel, using the electroless catalytic reduction process developed by Brenner and Riddell (ref. 6). This process produces a thin, uniform, continuous layer of metallic nickel on the surface of the steel. Autoradiographs of these specimens were then made. In every case the autoradiographs were darkened uniformly, indicating that no spurious effects were present which might give nonuniform exposure in the autoradiograph even though the radioactive isotope was, in fact, uniformly distributed over the surface of the specimen.

Seven additional specimens of 16-gage steel were prepared and pretreated as indicated in table III, after which they were treated for 5 minutes in the radioactive nickel solution. Radioassays were made on each specimen to evaluate the amount of nickel deposited, and autoradiographs were made to show the distribution of the deposit. The results indicate that the surface pretreatment of the specimen markedly affected the amount of nickel deposited. The radioassays indicate that the greatest amount of nickel was deposited on the sandblasted specimens, smaller but appreciable amounts were deposited on the polished specimens, and the least was deposited on the pickled specimens. One polished and one sandblasted specimen were pickled before the nickel-dip treatment. This pickling markedly reduced the amount of deposit in each case.

The autoradiographs, shown in figure 2, indicate that in every case the nickel was deposited from the nickel dip in a nonuniform layer. This would be expected, since, theoretically, substantial areas of iron must remain in contact with the solution for the galvanic plating reaction to proceed (ref. 7, discussion by Blum). The most surprising facts brought out by these autoradiographs were the striking differences in the patterns of the nickel deposits. On the sandblasted specimens, the nickel was apparently deposited on very small areas rather close together, the general

impression being similar to that produced by a grainy photographic film. In the cases of the polished and the pickled specimens, the pattern is much coarser.

There were two heavy scratches on specimen 5 before it was pickled. The autoradiograph showed that very heavy deposits occurred on these scratches. On the polished specimens there also seemed to be heavy deposits following a pattern of scratches.

The difference in the general pattern of deposit observed in pickled specimens 5 and 11 is real and more or less typical of what may be expected with pickled specimens. The total amount of nickel deposited is about the same in the two cases, as indicated by the radioassay counts reported in table III. Apparently, the heavy scratches on specimen 5 produced a relatively small total area of cathodic iron, on which the nickel deposited heavily, and a relatively large anodic area with no nickel deposit. In the case of specimen 11, the total area of cathodic iron is much greater, and a much lighter deposit of nickel occurred on the majority of this area.

These results confirm the findings of Wesley and Copson (ref. 7), who report that a sulfuric acid pickle shortly before immersion of the steel in the nickel bath resulted in an uneven sporadic nickel coating, presumably because the pickling formed large anodic areas. Wainer and Baldwin (ref. 8) also ascribe the variation in nickel deposit encountered in enameling practice to anodic passivity induced by the sulfuric acid pickle.

Although not of primary importance in this investigation, the variation in the amount of nickel deposited during the nickel dip with time of treatment may be of interest. These results are shown in figure 3 and serve to emphasize the effect of type of cleaning on the amount of deposit. When other conditions are constant, the amount of deposit is a function of the time of treatment. The different results obtained with the two methods of cleaning serve to emphasize the effects of the surface condition of the metal on the rate of nickel deposition.

Opposite sides of the same sheet of metal may sometimes have somewhat different surface properties, so that different amounts of nickel are deposited during pickling. An example of this is shown by the radioassay counts in table IV. Specimens T1 through T5 were cut from adjacent areas of the same sheet of metal, the identification numbers having been stamped on the side of the specimens corresponding to the "front" surface of the original sheet. The "back" side of the specimens gave in each case a higher reading, but there was no consistent percentage difference. This difference perhaps may be due to some cause such as the sheet's having been at the top or bottom of a pile during annealing.

The autoradiographs shown in figures 4(a) and 4(b) were made from $3\frac{1}{4}$ - by 4-inch specimens that were cleaned by pickling and sandblasting, respectively. The pickled specimen was dried after pickling. Several scratches were made with a diamond pencil in a crosshatch pattern on each specimen, after which the specimens were nickel dipped in the radioactive nickel solution. Radioassays made in unscratched areas after nickel dipping gave net counts of 23 per minute for the pickled specimen and 1,756 per minute for the sandblasted specimen. The autoradiographs, made with exposure times of 6 hours for the sandblasted specimen and 15 days for the pickled specimen, also show this marked difference in activity of the specimens.

A heavy deposit of nickel occurred at the scratches on the pickled specimen, but the deposit at the scratches on the sandblasted specimen is hardly noticeable in the autoradiograph. This suggests that cold-work of the steel may be responsible for the heavy deposit.

To check this hypothesis, specimens were treated with alkaline cleaner and cold-worked, as indicated in table V, by rolling and stretching, after which they were nickel dipped in radioactive nickel solution and counted. Rolling with polished rolls markedly decreased the amount of the nickel deposit. Pickling after rolling increased the amount of the deposit, but it was still less than that on the undeformed metal. Stretching increased the deposit slightly, but pickling after stretching decreased the deposit. Apparently, the rolling treatment markedly reduced the reactivity of the surface. This might be due in part to the reduction in available surface per unit area produced by rolling.

An autoradiograph of one of the stretched specimens revealed two interesting phenomena. There were several heavy deposits of nickel suggesting scratches, but casual observation of the specimen revealed no scratches at these areas. Microscopic examination of the specimen, however, did reveal the location of extremely fine scratches, forming the same pattern as the heavy deposit in the autoradiograph, that could be seen with the unaided eye when properly illuminated. Also, heavy deposits of nickel occurred in small areas in an irregular pattern, and similar areas appeared on the specimen. A photomicrograph and autoradiograph of this specimen are shown in figure 5.

The areas which appear dark in the photomicrograph are as clean as the surrounding metal but have slightly different reflection characteristics. They are not readily visible under ordinary diffuse illumination but are easily seen as dark areas when the specimen is illuminated obliquely by a light source of small area and viewed slightly off the direction of mirror reflection. Microscopic examination at magnifications up to 150 diameters revealed no differences in the surface texture of the metal in these areas. When the lot of steel from which this particular specimen was cut was examined, a thin light-brown deposit in a pattern similar to

that of the dark areas was found to occur on one side of a few sheets, and specimens containing these areas develop the dark areas after pickling. The nature of this brown deposit has not yet been established, but it may be formed by incipient rusting. The dark areas were apparently cathodic on some specimens and anodic on others, for in some cases heavy deposits occurred on them and in other cases no deposit of nickel was observed on the dark areas.

Effect of firing on nickel deposit.- Twelve 2- by 4-inch specimens were cut from 20-gage steel and marked for identification. Six specimens were cleaned by sandblasting and six, by pickling; then they were all nickel dipped in the radioactive nickel solution. Radioassays were made at known areas on all specimens, after which they were coated with enamel I-2 as indicated in table VI and then deenameled in molten sodium hydroxide at 800° F. This treatment removes the enamel completely but does not completely dissolve any iron oxide that may be present at the enamel-metal interface. After cooling to room temperature, the specimens were rinsed in hot running water and dried at 225° F, after which they were treated with warm 10-percent ammonium citrate solution, which dissolved and loosened the iron-oxide scale. They were then scrubbed in the ammonium citrate solution, rinsed in running water, and dried. Radioassays were made on the specimens in the same positions as before. A radioassay on a 2-milliliter aliquot of the 500 milliliters of sodium hydroxide used to deenamel all specimens gave a net count of 1 or 2 per minute, indicating practically zero activity. A radioassay on the ammonium citrate solution also indicated zero activity, but there was an insoluble radioactive residue in the bottom of the beaker of ammonium citrate.

The results indicate that no consistent effect upon the distribution of the nickel deposit was produced by the presence or absence of cobalt oxide in the enamel. There was, however, an effect of firing treatment as shown in table VI. In general, the amount of nickel remaining on the specimen after the treatment was reduced by increased severity of firing, but, even in the case of the overfired specimens, a major portion of the nickel remained on the surface of the steel. The observed decrease in count could be accounted for either by absorption of the beta rays by a thin film of oxide or other material not completely removed in the deenameling treatment, which does not appear likely, or by diffusion of the nickel into the iron during firing and deenameling of the specimens. The most likely explanation, however, is that some of the nickel was detached from the iron by undercutting during firing and was mechanically removed during the deenameling treatments. The radioactive insoluble residue in the ammonium citrate solution probably contains such particles.

Metallographic sections were made of other specimens that had been nickel dipped in radioactive nickel solution and then enameled. These sections were made at a very slight angle to the metal surface so as to reveal a larger area of any interfacial layers having a finite thickness.

The exposed surface is increased by a factor of about 50 in this case. Autoradiographs of the metallographic sections indicate that the nickel is concentrated at the enamel-metal interface, as shown in figure 6. There was no evidence in any of the autoradiographs of solution of the nickel into the enamel.

Additional specimens were mounted with the enamel-metal interface parallel to the surface of the mount. The enamel on the back of the specimen and most of the iron were ground off on a lap, and the remainder of the iron was removed by solution in iodine - potassium iodide reagent. This reagent dissolves metallic iron, nickel, and cobalt but not their oxides. After dissolving the iron, the reagent, containing the dissolved metal, was dried. Radioassays of the dried residue showed it to be quite radioactive. Similar radioassays on the chips indicated practically no radioactivity on most of the chips. The highest value on any chip was a net count of 115 per minute from a specimen which had a net count of 3,307 before enameling, as shown in table VII. These experiments indicate that the nickel from the nickel dip remains as metal at the enamel-metal interface and does not oxidize appreciably nor go into solution in the molten enamel during firing.

DISCUSSION

The experiments with radioactive cobalt indicate that the nickel from the nickel dip had only a minor effect on the amount of cobalt metal deposited at the enamel-metal interface during firing of a cobalt-bearing enamel on iron. However, these experiments did show that under otherwise identical conditions more cobalt was deposited on sandblasted than on pickled iron, particularly on underfired specimens, and that this difference tends to decrease with an increase in firing treatment. Similar but more pronounced differences were observed in the amount of nickel deposited from the nickel dip on sandblasted and pickled iron. This suggests that the cobalt is deposited from the molten enamel during firing by a galvanic process similar to that by which nickel is deposited from the nickel dip.

The observation that the nickel from the nickel dip is always deposited in a discontinuous layer is one that would be expected of a galvanic deposit. The marked difference in patterns produced on pickled and sandblasted iron seems to indicate that the surface of a pickled specimen is not so uniform in reactivity as that of a sandblasted specimen, or at least that the nonuniformities on a sandblasted specimen occur on a much smaller scale than do those on a pickled specimen.

The observation that heavy deposits of nickel occur on sandblasted specimens, on polished specimens, and at scratches on pickled specimens

indicates that metal that has been severely cold-worked is more easily
replaced by nickel in the nickel dip. This inference would also explain
why no exceptional deposit was noted at scratches on sandblasted specimens,
because the entire surface of such specimens has been severely cold-worked
and a heavy deposit occurs at all sandblasted areas. Theory would predict
that strained metal would be in a higher energy state relative to unstrained
metal and, hence, more rapidly dissolved. This theory would also explain
the effect of pickling in reducing the deposit obtained on sandblasted
and polished metal, for the strained metal would be removed more rapidly
than unstrained metal in the pickling treatment, reducing the activity
of the surface.

The stretching treatment of up to 10-percent deformation did not
appreciably increase the amount of nickel deposition and the rolling
treatment actually reduced it. Thus, if it is assumed that the state of
cold-work of the surface is for all practical purposes the controlling
factor in the rate of deposition, it would appear that the rolling and
stretching treatments produce a less intense localized surface distortion
than do sandblasting and scratching. However, the nickel pickling process
constitutes a heterogeneous surface chemical reaction from a water solu-
tion, involving the formation of iron ions at the metal surface, the
desorption of these through a water layer, the adsorption of nickel ions,
and the conversion of these to metallic nickel. Since any or all of
these processes may significantly affect the reaction rate and are sensi-
tive to surface conditions on the atomic scale, it is quite doubtful
whether the observations reported here should be attributed solely to
cold-working effects.

The observed increase in deposit on sandblasted, polished, and
scratched areas might also be due in part to the mechanical cleaning
action and the formation of fresh surfaces which are cleaner than those
produced in pickling. It is extremely difficult, however, to produce
mechanically a chemically clean surface without at the same time producing
appreciable cold-work in the surface.

The radioassays on the residues from the chemical separations of
enamel and metal after firing indicate that the nickel remains as metal
at the enamel-metal interface and is not diffused into the enamel. The
autoradiographs of the metallographic sections of fired specimens also
support this finding. This behavior conforms to the electrolytic corrosion
theory, since the more noble metal, nickel, in contact with the less noble
metal, iron, should be galvanically protected against oxidation so long
as there is any unoxidized iron present. The observed decrease in radio-
activity with increased firing treatment on specimens that were enameled
and deenameled might be caused by undercutting of small areas of the
nickel deposit, so that these metallic particles fell or were rubbed off
during the deenameling or ammonium citrate treatment and settled to the

bottom of these solutions. This explanation would account for the
radioactive residue found in the ammonium citrate beaker.

National Bureau of Standards,
     Washington, D. C., March 20, 1955.

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TABLE I.- PICKLING PROCEDURE

Step	Solution composition			Time in bath
	Material	Concentration, percent	Temp., °F	
1	Oakite cleaner	5.1	[a]212	20 min
2	Water	--------	[a]212	2 min
3	Water	--------	140	1 min
4	H_2SO_4	7	150 to 154	15 min
5	Water	--------	140	30 sec
6	$NiSO_4 \cdot \left(NH_4\right)_2 SO_4 \cdot 6H_2O$	2.4 (pH 3.0)	154 to 158	5 min
7	Water	--------	70	.3 to 4 sec
8	NaCN NaOH	.38 .20	122 to 126	15 sec
9	Water	--------	140	1 min
10	Transfer to dryer at 225° F			

[a]Boiling vigorously.

TABLE II.- COUNTS ON SPECIMENS ENAMELED WITH RADIOACTIVE

COBALT-BEARING ENAMEL AND THEN DEENAMELED

Specimens	Cleaned by	Nickel dip	Firing treatment		Net count[a]
			Time, min	Temp., ^oF	
P1	Pickling	Yes	4	1,450	3,240
P2	Pickling	Yes	4	1,575	11,800
P3	Pickling	Yes	6	1,750	20,400
P4	Pickling	No	4	1,450	3,940
P5	Pickling	No	4	1,575	10,700
P6	Pickling	No	6	1,750	21,600
S1	Sandblasting	Yes	4	1,450	8,840
S2	Sandblasting	Yes	4	1,575	13,100
S3	Sandblasting	Yes	6	1,750	21,500
S4	Sandblasting	No	4	1,450	8,870
S5	Sandblasting	No	4	1,575	14,600
S6	Sandblasting	No	6	1,750	24,700

[a]Above background.

TABLE III.- EFFECT OF SURFACE TREATMENT ON

AMOUNT OF NICKEL DEPOSITED IN NICKEL DIP[a]

Specimen	Cleaning treatment (b)	Net count	Distribution of deposit (c)
[d] 2	S + Pi	3,140	Uniform
3	S	2,610	Fine
4	S + Pi	809	Coarse
5	Pi	251	Very coarse
7	Po + Pi	252	Very coarse
9	Po	707	Very coarse
10	Po + E	653	Very coarse
11	Pi	272	Very coarse

[a]All specimens treated for 5 min in radioactive nickel solution.

[b]S, sandblast; Pi, pickle; Po, polish; E, etch.

[c]Evaluated by autoradiograph. See fig. 2.

[d]Nickel plated by Brenner-Riddell process (ref. 6).

TABLE IV.- EFFECT OF TIME OF TREATMENT ON

AMOUNT OF NICKEL DEPOSITED IN NICKEL DIP

Specimen	Cleaned by	Time of treatment, min	Net count	
			Front	Back
T1	Pickling	1	26	49
T2	Pickling	2	42	50
T3	Pickling	3	105	134
T4	Pickling	4	111	172
T5	Pickling	5	151	215

TABLE V.- NICKEL DEPOSITION ON COLD-WORKED SPECIMENS

Specimen	Deformed[a]		Treatment after deformation	Net count
	By	Amount, percent		
0	None	0	None	166
1	Rolling	2	None	177
2	Rolling	4	None	90
3	Rolling	6	None	58
4	Rolling	8	None	84
5	Rolling	10	None	9
0-P	None	0	Pickled	758
1-P	Rolling	2	Pickled	436
2-P	Rolling	4	Pickled	616
3-P	Rolling	6	Pickled	584
4-P	Rolling	8	Pickled	707
5-P	Rolling	10	Pickled	580
[b] 1 St.	Stretching	10	Pickled	594
[b] 2 St.	Stretching	10	Pickled	686
[b] 3 St.	Stretching	10	None	871
[b] 4 St.	Stretching	10	None	840

[a]All specimens were treated with alkaline cleaner (steps 1, 2, and 3, table I) before deformation.

[b]Pickled before treatment.

TABLE VI.- COUNTS ON SPECIMENS TREATED WITH RADIOACTIVE

NICKEL DIP, ENAMELED, AND THEN DEENAMELED

Specimen	Net count on bare iron	Enamel type (a)	Firing conditions		Net count on deenameled iron	Percent of original
			Time, min	Temp., °F		
Pickled specimens						
P1	1,033	CF	4	1,450	696	67.4
P2	1,416	CF	4	1,575	1,100	77.6
P3	898	CF	6	1,750	488	54.3
P4	926	CB	4	1,450	680	83.4
P5	674	CB	4	1,575	494	73.3
P6	780	CB	6	1,750	501	64.2
Sandblasted specimens						
S1	6,440	CF	4	1,450	5,900	91.7
S2	5,665	CF	4	1,575	4,850	85.6
S3	7,462	CF	6	1,750	6,100	81.7
S4	6,838	CB	4	1,450	6,430	94.0
S5	6,185	CB	4	1,575	5,400	87.4
S6	6,373	CB	6	1,750	4,970	78.0

[a]CF, cobalt-free; CB, cobalt-bearing.

TABLE VII.- RADIOASSAYS AFTER CHEMICAL

SEPARATION OF ENAMEL AND METAL

Specimen	Net count before enameling	Coating type (a)	Firing conditions (b)	Net count on	
				Chip	Residue from I_2-KI solution
14	3,307	CB	N	115	1,890
15	2,130	CF	N	12	2,110
17	3,844	CB	U	59	1,510
18	3,676	CB	O	17	1,620
19	3,091	CF	U	104	1,800
20	3,608	CF	O	61	1,800

[a]CB, cobalt-bearing; CF, cobalt-free.

[b]N, 4 min at 1,575° F; U, 4 min at 1,450° F; O, 6 min at 1,750° F.
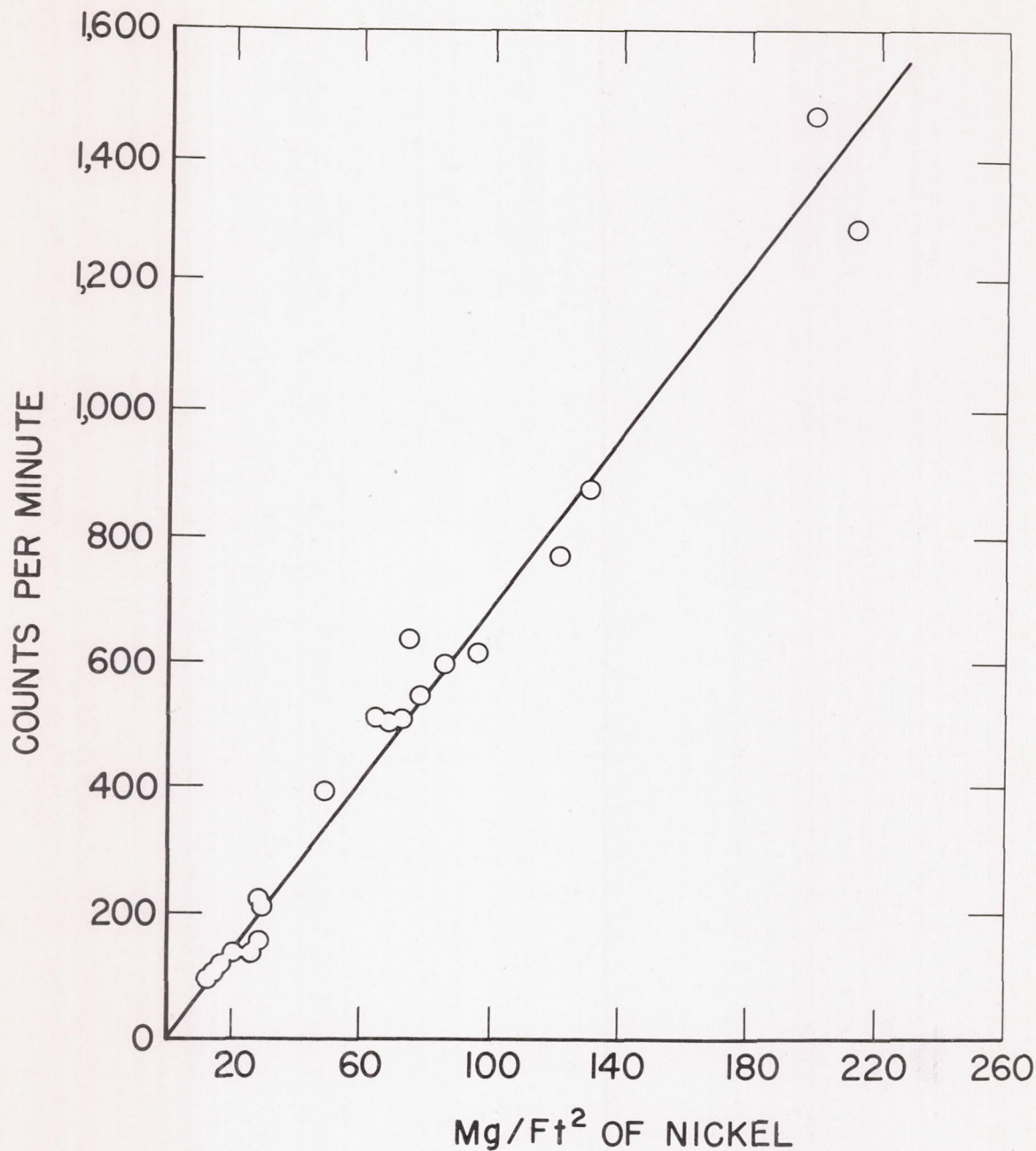
Figure 1.- Relation of nickel 63 activity count to chemical analysis. Counts obtained on specimens nickel dipped in radioactive nickel solution are plotted as a function of weight of nickel present in same marked area as determined chemically.
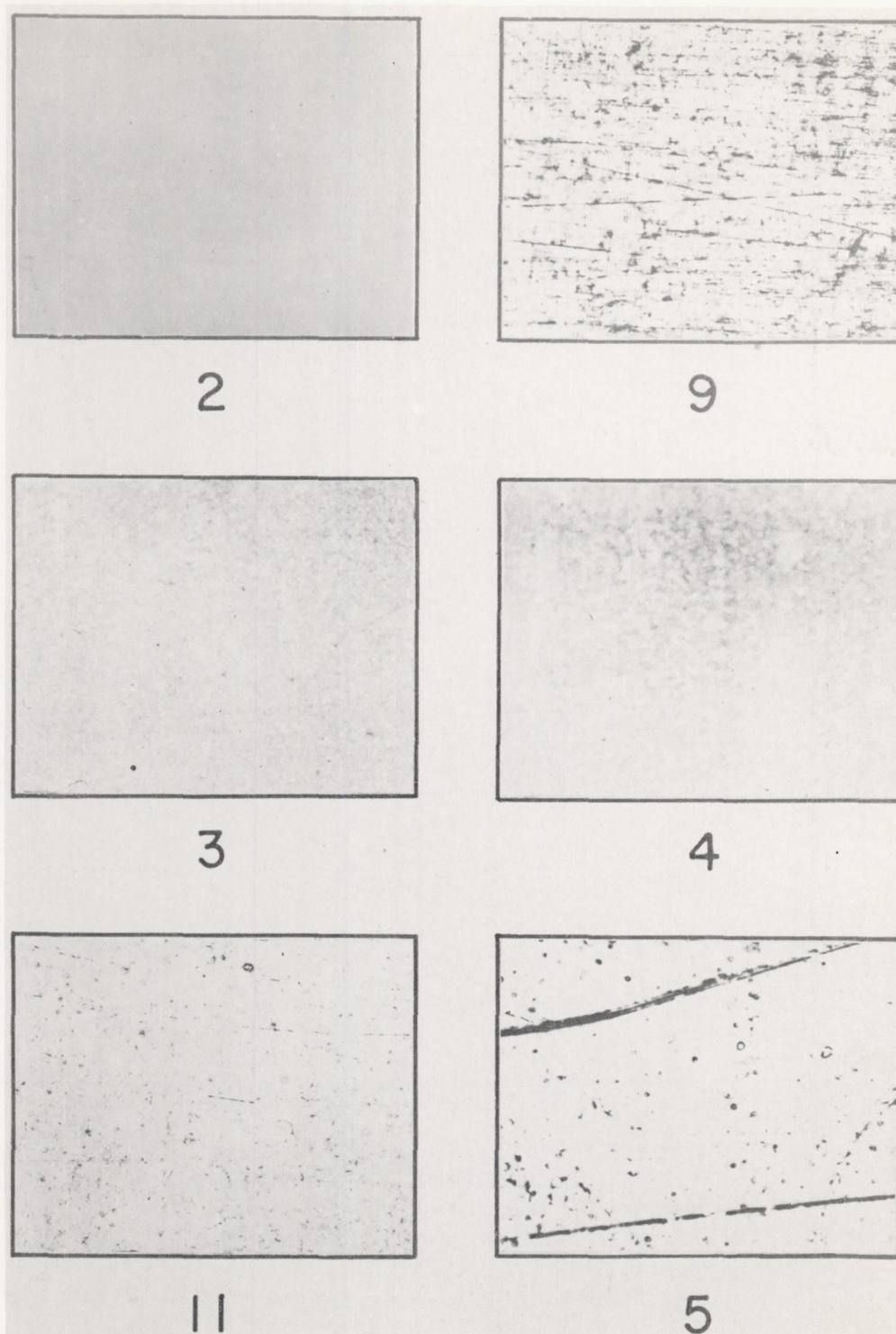
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Figure 2.- Autoradiographs (X4) of specimens described in table III. The two heavy lines on autoradiograph of specimen 5 occur where scratches were present on specimen before pickling.
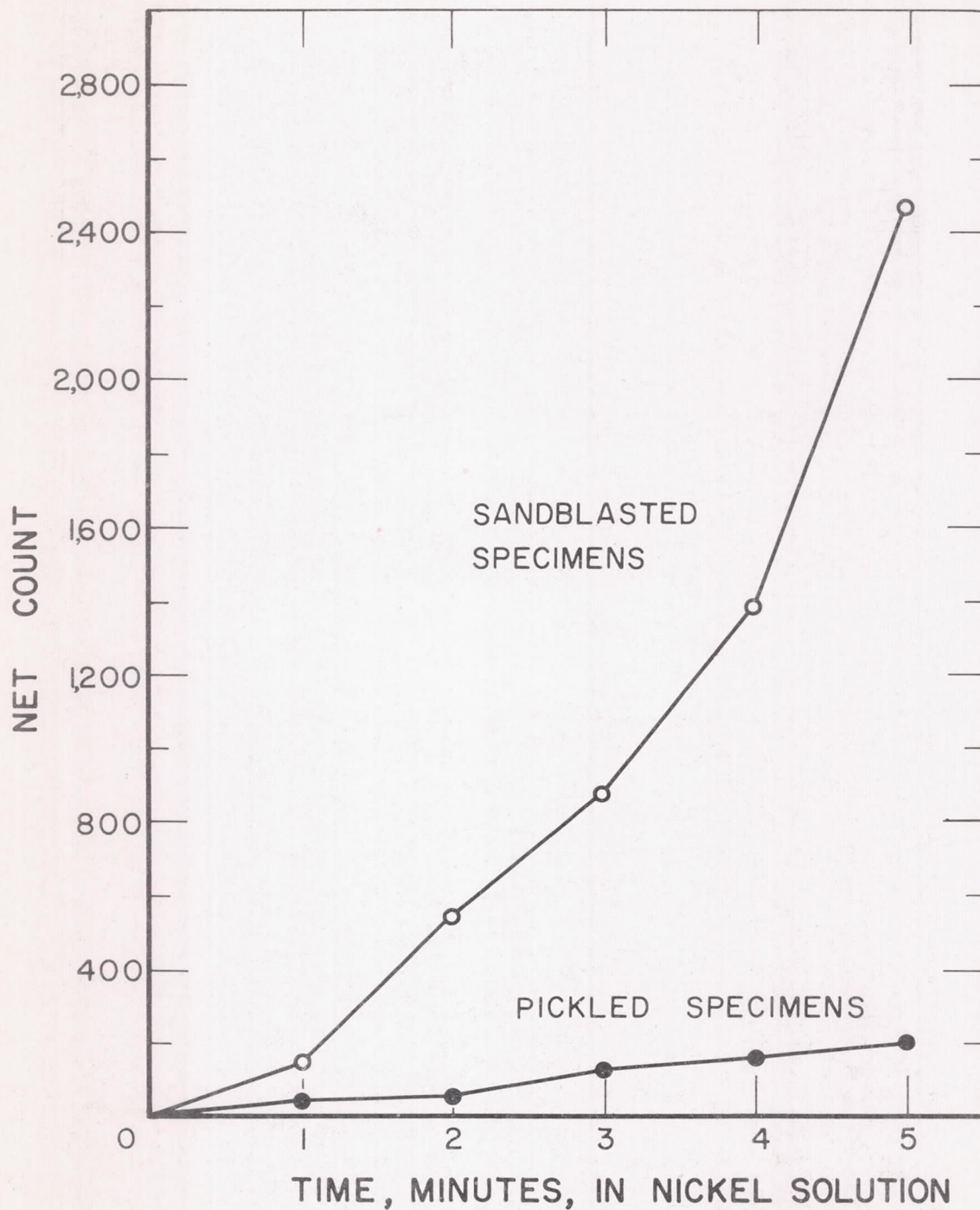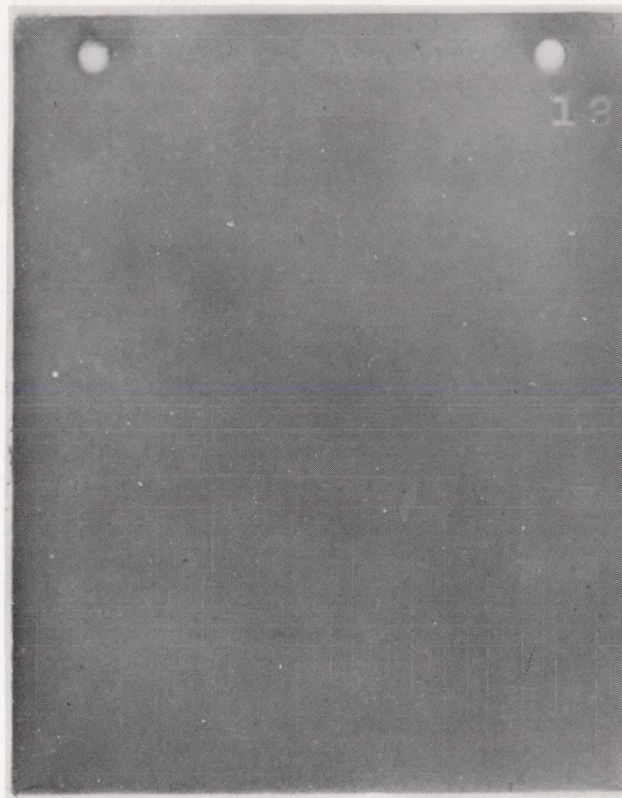
Figure 3.- Effect of cleaning treatment on amount of nickel deposited in nickel dip.

(a) Pickled specimen.
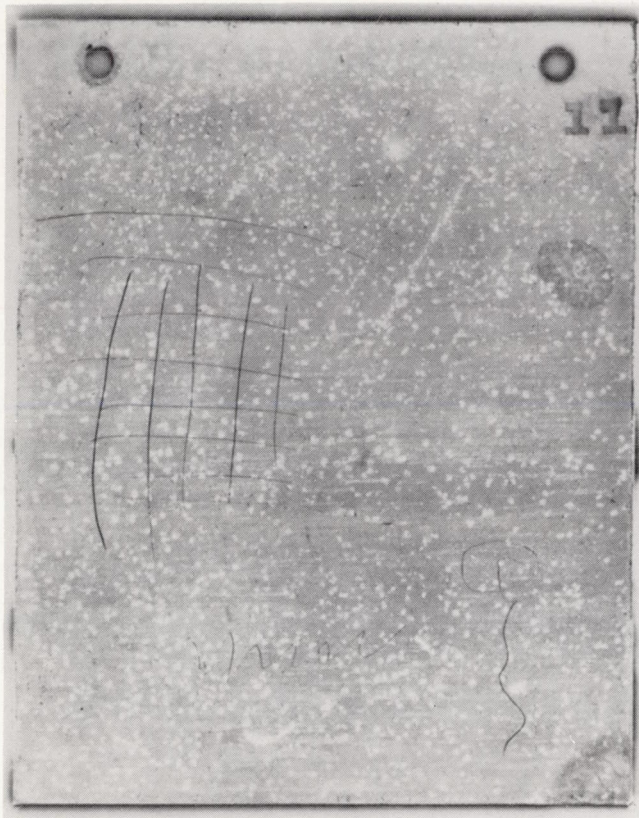
(b) Sandblasted specimen.

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Figure 4.- Autoradiographs, natural size, of pickled and sandblasted specimens after nickel dipping in radioactive nickel solution. Both specimens were scratched with a diamond pencil in a cross-hatch pattern before nickel dipping, but heavy deposits occurred only on scratched areas of pickled specimen.
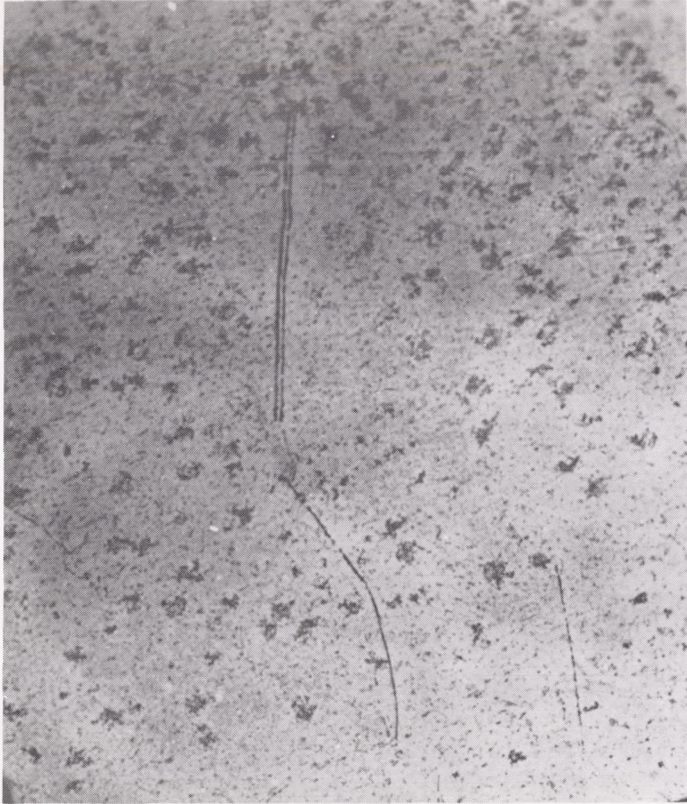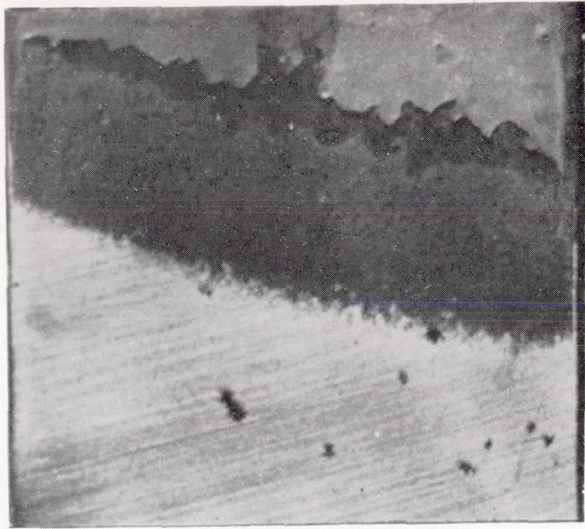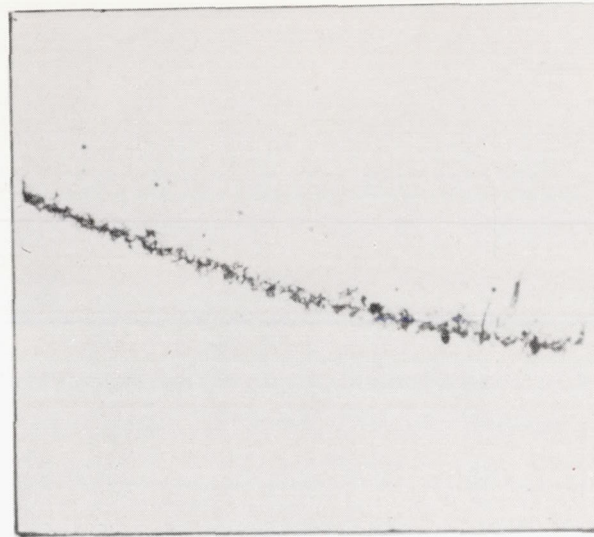
(a) Autoradiograph.
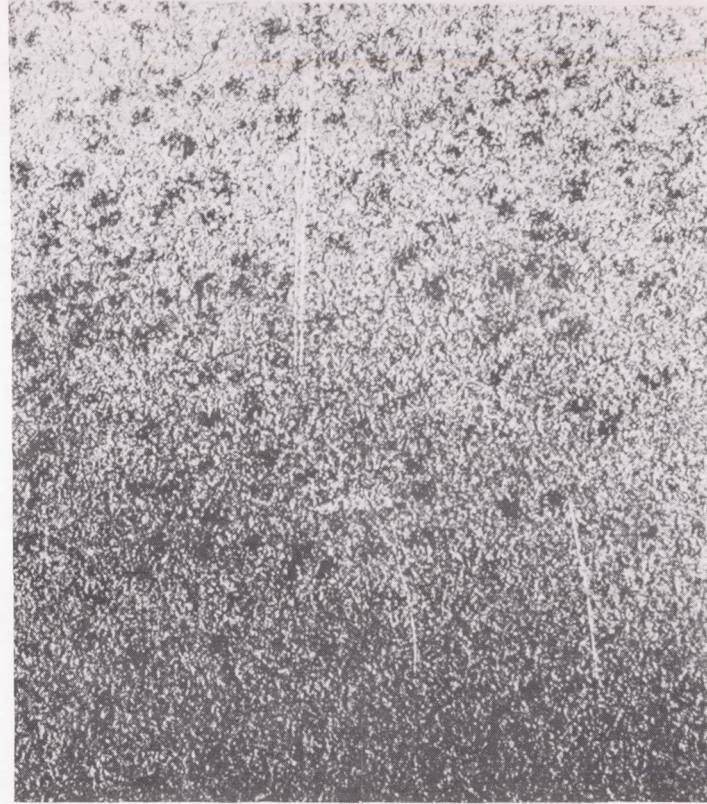
(b) Photomicrograph.

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Figure 5.- Autoradiograph and photomicrograph, both X4, of specimen which had been stretched in tension and then nickel dipped in radioactive nickel solution.

(a) Photomicrograph.   (b) Autoradiograph.

Figure 6.- Photomicrograph and autoradiograph, both X5, of tapered metallographic section of porcelain-enameled steel specimen that had been nickel dipped in radioactive nickel solution before enameling. There is no evidence of migration of nickel into enamel or metal. The few large black dots on autoradiograph above line of interface occur at bubbles in enamel which penetrated through to metal, exposing radioactive nickel on surface of steel.