DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON

THE PROTECTIVE VALUE OF NICKEL PLATING ON
IRON AND STEEL

This paper includes the methods of study and the conclusions reached in an investigation of this subject at the Bureau of Standards. Further details will be published in an article by C. T. Thomas and W. Blum to be presented at the September 1925 meeting of the American Electrochemical Society which will be published in Volume 48 of their Transactions.

1 - General Principles

It has long been recognized that nickel plating does not exert the same kind of protection against the corrosion of iron and steel, as does zinc plating. The protective value of the zinc depends upon the fact that zinc has a greater "solution pressure" or tendency to dissolve, than does iron. When therefore zinc is in contact with iron, in the presence of moisture, an electrolytic cell is formed, in which the zinc is the anode, or dissolving electrode, and the iron is the cathode. The presence of zinc will therefore prevent iron from dissolving or corroding upon any small exposed areas.

Nickel however has a lower solution pressure than iron, and when nickel and iron are in contact in the presence of moisture, the corrosion of the iron is actually accelerated by the presence of the nickel. In view of these facts it is obvious that in order to completely protect iron against corrosion by nickel plating, the latter must be free from pores. The research therefore consisted principally in the determination of the conditions which led to the production of the most nearly impervious nickel deposits.

Among the possible causes of porosity in nickel coatings, are:

(a) The presence of defects in the base metal, such as blow-holes, or particles of slag, oxides, or sand from the molds. Plating does not usually cover such defects, and it may accentuate them. To eliminate such failures it is necessary to use proper care in the manufacture and selection of the steel.

(b) The presence of rust or other foreign materials on the surface. These may be removed by appropriate methods of cleaning and pickling.

(c) The presence of suspended matter in the plating solutions, which may lodge upon the cathodes. Such materials can usually be removed by filtration.

(d) The presence of gas bubbles on the surface, consisting either of hydrogen or of air, and the consequent formation of pits. The tendency for liberation of hydrogen and of

pitting is partly determined by the acidity of the nickel
bath, but is also undoubtedly influenced by other causes.

II - Methods of Plating

The experiments were made upon small pieces of cold rolled
sheet steel, 4" x 4" (10 x 10 cm). Six of these were plated
at the same time upon a rack with approximately uniform cur-
rent distribution. They were cleaned before plating by a
great variety of processes and combinations, some of which
will be referred to later. Pure (99%+) nickel anodes were
used. Four different nickel solutions were applied under
different operating conditions. At least twelve plates
were made under each set of conditions.

III - Methods of Testing

A - Corrosion Tests

If the protective value of the nickel coatings is deter-
mined principally by their porosity, any conclusive test
for porosity should indicate the relative protective value
of the coatings. In making any porosity or corrosion test,
it is necessary to have the surface entirely free from grease.
In buffing operations, the pores in the nickel may become
filled with grease, and thereby the apparent protective value
will be increased. In actual service, the presence of this
grease may be an advantage, but in testing buffed coatings,
it is necessary to clean the surface completely, for example
in an electrolytic cleaner, in order to get reproducible re-

sults.

In this study the nickel plated samples were tested by
four methods, and the average of the four results was taken
as a measure of the relative protective value of the coat-
ings produced under any given set of conditions. In order
to average the results of different tests it was necessary
to adopt arbitrary units, which were so chosen that the
average of all the results by each method was about the same.
The units used are defined under each of the following tests.

1 - Ferricyanide Test (F). The solution was prepared
as follows. About 1.3 oz/gal (10 g/L) of agar-agar (a vege-
table substance resembling gelatin) was dissolved in boiling
water and 1.3 oz/gal (10 g/L) of sodium chloride and 0.13
oz/gal (1 g/L) of potassium ferricyanide were added. On
cooling the solution set to a jelly, which became liquid
upon being again warmed.

When the nickel plated sheets are dipped into this solu-
tion and allowed to drain, blue spots appear within a few
minutes at any points where iron is exposed. For purposes
of comparison the number of spots on each side of the plate
within a circle 2" (5 cm) in diameter was recorded. A small
number of spots indicated a better coating than a large num-
ber. In order to obtain a rating which would correspond to
the value of the nickel coating, 100 was divided by the
average number of spots present on the two sides. Thus if
within the circle, there were 19 spots on one side, and 15

spots on the other side, the average was 17 spots, and the

ferricyanide rating was $\frac{100}{17} = 5.9$.

2 - <u>Salt Spray Test</u> (SS). The samples were subjected to
the spray of a twenty per cent solution of sodium chloride,
by the method described in Circular 80 of the Bureau of
Standards. Failure was judged by the appearance of rust
spots that could be readily seen at a distance of about
.3 feet (1 meter). The results were expressed in terms of
six hour periods. Thus if a specimen failed in 24 hours,
it had a salt spray rating of 4.

3 - <u>Intermittent Immersion Test</u> (I.I.). In this test
the samples were attached to the spokes of a wheel, which
rotated once in fifteen minutes. During one minute of each
"cycle" the specimen was immersed in sodium chloride solu-
tion, (4 oz/gal or 30 g/L) and during the remaining 14
minutes it was in the air. Failure was defined by the same
appearance as in the salt spray test, and was recorded in
terms of the number of fifteen minute cycles.

4 - <u>Atmospheric Exposure Test</u> (A.E.). The samples were
exposed to the atmosphere upon the roof of one of the
Bureau of Standards buildings in Washington, until rust ap-
peared which was plainly visible at a distance of about
3 feet (1 meter). The results were expressed in "weeks"
of continuous exposure.

B - Adhesion Tests

The adhesion of the nickel plating was measured roughly
by observing whether the nickel peeled when the specimen
was tested in an Erichsen penetration machine, in which a
plunger is forced against the sheet till rupture occurs.
The test was not very conclusive, as all specimens stood
it except those in which the preparatory cleaning was known
to be defective or in which a large amount of iron was pres-
ent in the bath and the deposit.

C - Hardness Tests

The relative hardness, or more strictly the resistance
to abrasion, was determined by scratch hardness tests. In
this method a sapphire (or a diamond) point is drawn across
the surface under a definite small load, and the width of
the scratch is measured with a microscope. The hardest de-
posits yield the narrowest scratches.

IV - Results

It was found that the most important factor in determin-
ing the protective value of the coating is the thickness
of the deposit. Thus it was found that the average rating
of all the coatings which were 0.00025" (0.006 mm) thick,
was 1.4; of those which were 0.0005" (0.013 mm) thick, it
was 3.9; and of those that were 0.001" (0.025 mm) it was
10.2. In other words, the protective value, as measured
by the average of the four tests used, increased more than
proportionally to the thickness of the deposit.

It was not found possible by any methods of preparation
or plating to produce relatively thin deposits of nickel
(such as 0.00025" or 0.006 mm) which are nearly impervious
or which furnish satisfactory protection against corrosion.
The conditions of preparation which yielded results slightly
above the average were (1) pumice scrubbing, (2) pickling
with concentrated nitric acid, (3) anode pickling in con-
centrated sulphuric acid, (4) anode cleaning in alkali, and
(5) a preliminary rinse in a very weak sodium carbonate solu-
tion just before plating. Even by these methods however the
improvement was only slight, and in no way comparable to the
effect produced by increasing the thickness of the deposit.
Cathode electrolytic cleaning did not yield as good results
as did the methods just referred to. Oxidizing agents such
as hydrogen peroxide and potassium permanganate do not great-
ly decrease the porosity and they reduce the throwing power,
especially at low current densities. Iron when present
in appreciable amounts, especially as suspended sludge, in-
creases the porosity of the deposits.

The use of copper, either prior to the nickel plating, or
between an initial and final layer of nickel, was found to
increase slightly the protective value, especially of the
thicker coatings, such as those with a total thickness of
about 0.001" (0.025 mm). The application of zinc or cadmium
coatings prior to the nickel plating greatly increases the
protective value, which however is not as good as if the zinc

or cadmium were applied without any nickel upon it. Although
the deposits with zinc or cadmium under the nickel do not
readily show iron rust, they do become coated with white
spots, and there is sometimes a tendency toward peeling of
the nickel.

The hardness measurements showed that the hardest de-
posits are produced at a high current density, a low tem-
perature, and with a high content of sodium sulphate in
the bath. Warm solutions, especially those containing con-
siderable chloride, usually produce softer deposits.

V - Conclusions

It is not practicable by any of the methods tried, to pro-
duce entirely impervious nickel deposits. No commercial de-
posits of nickel tested by this Bureau have been found to be
entirely free from porosity. By increasing the total thick-
ness of nickel or of nickel plus copper, to at least 0.001"
(0.025 mm) fairly satisfactory protection can be obtained.
To produce this average thickness of nickel it requires
about 20 ampere hours per square foot. Thus if the average
current density is 10 amp./sq.ft., two hours will be required.

The current density may be increased and the time of plating
correspondingly shortened by using a high concentration of
nickel salt, a relatively low pH, moderate movement of the
cathodes, freedom from suspended matter, relatively high
temperature and pure nickel anodes.