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"THROWING POWER" IN COPPER AND NICKEL DEPOSITION

1 - Introduction

In both electroplating and electroforming[1] it is desirable

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[1] The production or reproduction of articles by electrodeposition, including electrotyping and the production of tubes, sheets, etc.

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to secure a deposit of uniform thickness, but difficult to do so upon irregularly shaped or recessed surfaces. The solutions from which the most nearly uniform metal distribution can be secured, are said to possess good "throwing power". The purpose of this paper is to explain the principles which govern the throwing power of solutions, and to illustrate the application of these principles in the deposition of copper and nickel[2].

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[2] Further details will be found in an article by H. E. Haring and W. Blum - Trans. Am. Electrochem. Soc. Vol. 44, 313, (1923) and one by H. E. Haring, Vol. 46, 107, (1924).

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2 - Principles

Whenever an irregularly shaped article is made the cathode in a plating solution, certain parts are closer to the anode than are others. The resistance through the solution from the anode to a near part is less than to a far part, and the current density (e.g. in amperes per square foot) will be greater upon the near part than upon the far part. If then the resistance through the solution were the only factor which determined the proportion of the current passing to the near and the far points, we would have a certain distribution of the current on the cathode, which we may designate as the "primary current distribution". Thus if the resistance to a near point were only one fifth of that to the far point, the current density upon the near point would be five times that
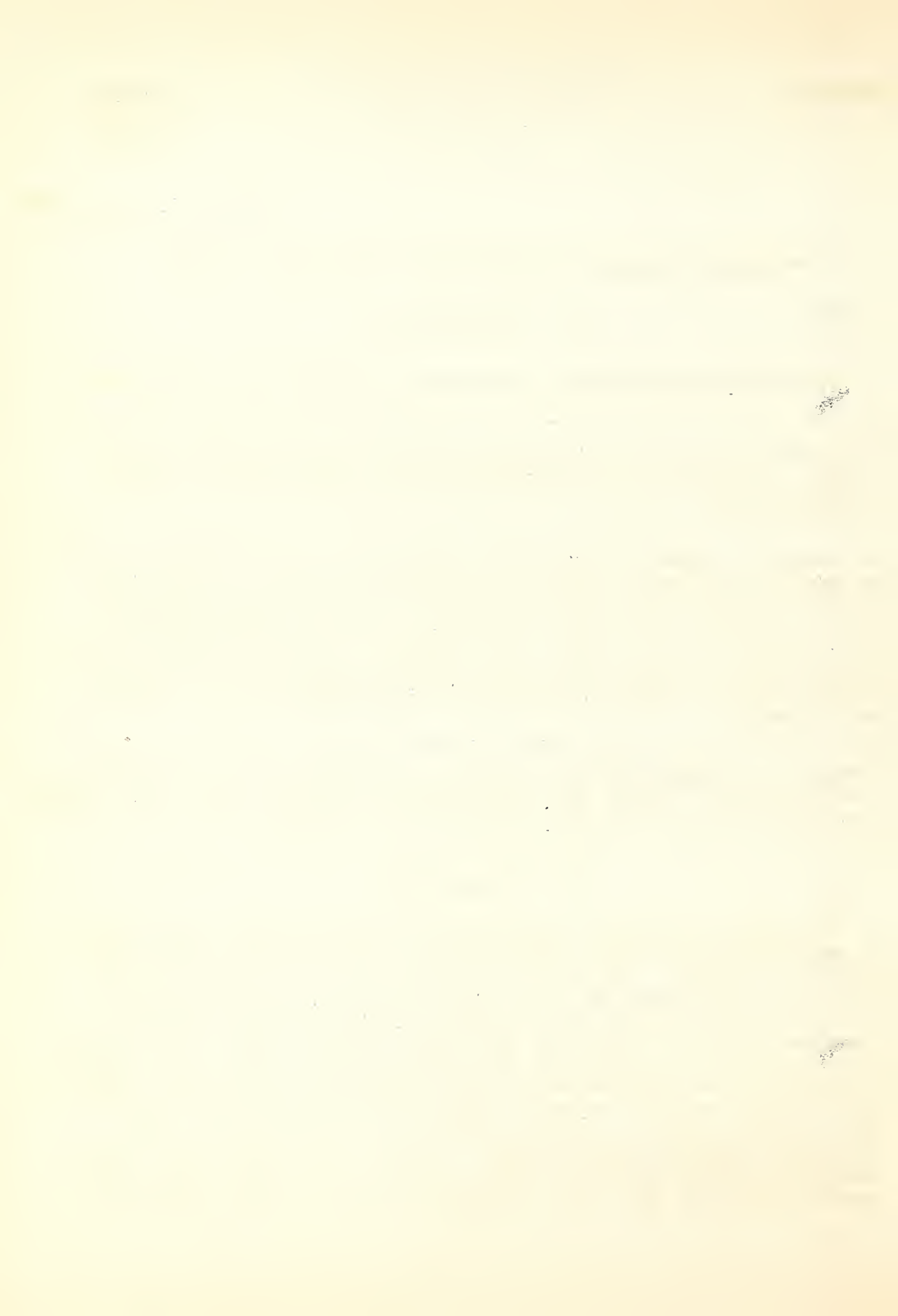
on the far point; in which case the primary current distribution ratio on these two parts would be 5 to 1. This ratio represents the current distribution that would be expected from the shape of the article and its position with respect to the anodes and the other cathodes in the bath.

Whenever current is passed through a metal salt solution and metal is deposited upon the cathode, the concentration of the metal salt (and metal ions) is reduced, to some extent at least, in the film of solution immediately adjacent to the cathode surface, because a fresh supply of the metal salt is not brought up as rapidly as it is consumed. For a given solution, the metal concentration is depleted to a greater degree as the current density is increased. It requires a higher potential at the cathode surface to deposit metal from a dilute than from a concentrated solution, hence it requires a higher potential to deposit metal at a high than at a low current density. The increase in cathode potential required at any given current density, above the equilibrium potential when no current is flowing, is called _polarization_, which when caused by such conditions as the above is "concentration polarization".

As a result of this polarization, which is greatest upon the points with highest current density, the current density at the near point is less than would be expected simply from the resistance through the solution, and hence the "secondary" or actual current distribution ratio is always more nearly uniform than the primary ratio. Thus, e.g. if the primary ratio is 5 to 1, the secondary current ratio may become 4.5 to 1 as a result of polarization.

If in any plating bath a certain voltage or potential is applied, it may for convenience be divided into three parts, (a) the potential necessary to cause the anode to pass into solution, which is determined by the "anode polarization", caused by an increase in the metal and metal ion concentration near the anode; (b) the potential required to overcome the resistance of the solution, and (c) the potential necessary to deposit the metal, as determined by the cathode polarization. For present purposes we will leave the anode potential out of consideration, as it has no direct effect on throwing power. If then the total potential is considered as equal to the sum of (b) and (c), the relative effect of (c), the cathode polarization, can be increased by decreasing (b), i.e. by increasing the conductivity of the solution (or decreasing the resistivity).

We are interested however not so much in the current distribution upon different parts of the cathode as upon the amounts (or thicknesses) of the metal deposits on these parts. When a current is passed through a plating solution it may be only partly used in depositing metal, the remainder being

usually consumed in the liberation of hydrogen. The cathode
efficiency is the percentage of the current used to deposit
metal. If this is much less than 100 per cent, hydrogen is
also liberated, as indicated by the "gassing" at the cathode.
If the cathode efficiency is 100 per cent or is equal at both
high and low current densities, the weights and thicknesses
of the metal deposits will be proportional to the current
densities. If however the cathode efficiency is higher at a
low current density than at a high current density (as in cop-
per solutions) the deposit at the near point will be relative-
ly thinner than corresponds to the secondary current ratio,
e.g. the metal ratio may be 4 to 1 when the actual current
ratio is 4.5 to 1. If, however, as in nickel deposition, the
cathode efficiency is less at a low than at a high current
density, the metal distribution will be less uniform than cor-
responds to the actual current ratio, e.g. it may be 6 to 1
when the actual current ratio is 4.5 to 1.

From the above considerations we may define throwing power
as "the deviation in per cent of the metal distribution ratio
from the primary current distribution ratio". Thus if the
primary ratio is 5 to 1, and the metal ratio is 4 to 1, the
distribution has been improved to the extent of $\frac{5-4}{5} = \frac{1}{5}$ or
20 per cent, which represents the throwing power. If however
the metal ratio is 6 to 1, it is less uniform than the primary
ratio, hence the throwing power is negative, in this case -20
per cent.

The throwing power as thus defined depends only upon three
factors, (a) the cathode polarization, (b) the conductivity
(or resistivity) of the solution, and (c) the cathode effi-
ciency.

Of these factors, the one that largely determines the be-
havior of any given type of solution is the polarization.
The rate of change of polarization with current density dif-
fers greatly in different solutions. Thus e.g. solutions of
lead fluoborate, or of silver nitrate, have very little polari-
zation and hence very poor throwing power. Solutions of copper,
nickel or zinc sulphate have moderate polarization and only
fair throwing power. The cyanide solutions of copper, zinc
and silver have very marked polarization and very good throw-
ing power.

The conductivity is only effective in increasing throwing
power provided there is an appreciable polarization.

In copper sulphate solutions the cathode efficiency is
usually nearly 100 per cent and therefore it has little
effect upon the throwing power. In copper cyanide solutions
the efficiency is less at a high than at a low current density
and therefore it improves the throwing power above what would

BE expected from the secondary current ratio. In nickel
solutions, however, the efficiency is less at low than at
high current densities, therefore the metal ratio is less
uniform than the actual current ratio, and the throwing
power is decreased.

3 - Apparatus and Method of Measurement

In order to measure throwing power, a simple apparatus,
shown in the attached figure, was devised. This consists of
a hard rubber box, the inside dimensions of which (up to the
height of the solution) are 10 x 10 x 60 cm (4 x 4 x 24 inches).
The anode, which consists of gauze of the metal to be used, is
in a slot 10 cm (4 in.) from one brass cathode (the "near
plate") and 50 cm (20 in.) from the other (the "far plate").
By having each cathode fill the entire cross section of the
solution, a practically uniform current density is maintained
over the entire area of each cathode. This condition is es-
sential for obtaining definite and reproducible results. The
two cathodes are connected by a heavy brass rod, so that they
represent in effect the two corresponding parts of any ir-
regularly shaped article.

To measure the throwing power, the box is filled to a
depth of 10 cm (4 in.) which requires 6 liters (about 1.6
gallons) of the solution to be tested. The two cathode
plates are carefully cleaned and dried, and weighed on a
fairly sensitive balance capable of weighing up to 50 grams
with an accuracy of 1 milligram. They are then inserted in
the appropriate slots and connected, and any desired current
is passed through the solution for a definite period. The
plates are then rinsed and dried and reweighed. The throwing
power is calculated from the weights of the deposits on the
two plates. Suppose the following data were obtained.

$$\begin{aligned}
\text{Near plate + deposit} &= 34.545 \text{ g} \\
\underline{\text{Wt. of near plate}} &= \underline{34.100} \\
\text{Deposit on near plate} &= 0.445
\end{aligned}$$

$$\begin{aligned}
\text{Far plate + deposit} &= 34.168 \\
\underline{\text{Wt. of far plate}} &= \underline{34.062} \\
\text{Deposit on far plate} &= 0.106
\end{aligned}$$

"Metal ratio" (ratio of weights on the two plates) =
$$\frac{0.445}{0.106} = 4.20$$

Primary ratio (as used in box) = 5.00. Deviation of metal
ratio from primary ratio = 5.00 - 4.20 = 0.80. Throwing
power (deviation in percent) =
$$\frac{0.80}{5.00} \times 100 = +16\%.$$

If in another solution (e.g. nickel) the deposits on the two
plates weighed 0.432 g and 0.080 g respectively, the metal
ratio is

$$\frac{0.432}{0.080} = 5.40.$$

Therefore the distribution is less uniform than the primary
ratio, and the throwing power is

$$- \frac{0.40}{5.00} \times 100 = -8\%.$$

The results for throwing power included in this paper were
obtained in this box, with a primary ratio of 5 to 1. It
should be borne in mind that the throwing power box is merely
a diagrammatic representation of an irregularly shaped object,
and that the results obtained are of value only in showing
the relative effects of different conditions. It is not
possible by any practicable means to measure the actual cur-
rent distribution on an irregularly shaped object, or to pre-
dict the metal distribution upon it. We can however from such
results as are given here, predict whether the throwing power
and metal distribution will be improved by changing any given
condition of operation. This may be illustrated by an actual
experiment.

It was found (Table 4) that under certain conditions a
nickel solution containing ammonium chloride had a throwing
power of +16.4 per cent, while one containing sodium fluoride
instead of ammonium chloride had a throwing power of -59 per
cent. A number of brass shaving soap boxes about 3 cm (1.2 in.)
in diameter and 5.5 cm (2.2 in.) deep were plated under the
same conditions in each of these solutions. The amount of
nickel deposited upon the inside of the bottom and the ad-
jacent parts, was determined. It was found that those plated
in the solution containing ammonium chloride had 1.7 times as
much nickel on the area tested, as those in the fluoride solu-
tion, which fact is in accord with the above results for the
relative throwing powers of the two solutions.

4 - Results Obtained

For each type of solution a definite composition and defin-
ite conditions of operation were selected as "standard", to
serve as a basis of comparison. It is not implied, however,
that such a solution and conditions are necessarily desirable
for any given purpose.

The results for copper sulphate, copper cyanide, and nickel
solutions will be explained. Even though the same factors af-
fect the throwing power in each case, it is preferable to dis-
cuss the three types of solution separately, as the relative
importance of the different factors varies greatly.

A - Copper Sulphate Solutions

(1)- <u>Current Density</u> - The throwing power is decreased as the current density is raised.

(2)- <u>Temperature</u> - Warming the solution decreases throwing power. Although it improves the conductivity, it reduces the polarization to a greater extent.

(3)- <u>Agitation</u>- Stirring the solution, e.g. with air, decreases the throwing power. In an acid copper solution the throwing power would be improved if it were possible to agitate the solution in the recesses, i.e. the parts with a low current density, without stirring the solution on the exposed parts.

(4)- <u>Metal and Acid Concentration</u> - The throwing power is decreased by the addition of copper sulphate, which reduces the polarization; and increased by the addition of sulphuric acid, which improves the conductivity.

(5)- <u>Addition Agents</u> - Colloidal addition agents such as dextrin and gelatin, increase the throwing power, especially at low current densities.

B - Copper Cyanide Solutions

The most significant result of the experiments on copper cyanide solutions is that in them the throwing power is from 30 to 40 per cent, as compared with 2 to 18 per cent in copper sulphate solutions. This difference is in agreement with the well known superior throwing power of the cyanide solutions.

The effects of the various conditions are less marked in the cyanide than in the sulphate baths. The throwing power is improved slightly by increasing either the current density or the temperature.

C - Nickel Solutions

In nickel solutions the throwing power is frequently negative because, as previously mentioned, the cathode efficiency is lower at a low than at a high current density. In order to improve the cathode efficiency and the throwing power, it is desirable to increase the nickel content (or more strictly speaking the nickel ion content) of the solution, and to decrease the acidity (the hydrogen ion content) i.e. to increase the pH of the solution.

The effects of the principal factors on the throwing power are as follows.

(1) <u>Current Density</u> - An increase in current density causes the throwing power to approach zero, whether it is positive

or negative at low current densities. At first it might
therefore appear that at the usual average current densities
all nickel solutions would have the same throwing power.
Actually however when recessed articles are plated, rela-
tively low average current densities are used, or at least
on the farthest parts the current density is low.

(2) Temperature – Warming the solution decreases throwing
power because it lowers the efficiency at low current densi-
ties.

(3) Agitation – The chief advantage of agitation in plat-
ing is that it permits the use of higher current densities,
i.e. of more rapid plating. If the solution were agitated
equally over the entire surface of the article, the throwing
power would be decreased. In practice however the agitation,
e.g. in a conveyor tank, is more marked on the exposed parts,
on which the current density is highest. To represent these
conditions ("local agitation") the solution close to the near
plate was agitated but not that at the far plate. The results
show that such agitation improves the throwing power.

(4) Acidity and Nickel Concentration – As previously indi-
cated, the throwing power may be improved by increasing the
nickel content or decreasing the acidity (increasing the pH).

(5) Effect of Added Salts – All chlorides used improve the
throwing power, while ammonium sulphate (which is present in
the "double" nickel salt) and sodium fluoride each decrease the
throwing power. Large additions of sodium sulphate or magnesium
sulphate greatly increase the throwing power.

(6) Nickel Chloride Solutions – Solutions containing all
the nickel as chloride (such as were used in the early days
of plating) possess very good throwing power. The deposits
obtained by us were darker than normal, so that further work
will be needed before the use of such solutions could be jus-
tified.

(7) Additions to Nickel Baths.

a – Sodium Citrate. This salt, often used in nickel plat-
ing on zinc, slightly improves throwing power, but not suffi-
ciently to warrant its addition for this purpose.

b – Dextrin. Dextrin is a typical colloid, present as an
impurity in commercial glucose and occasionally added in that
form to nickel baths. While it slightly improves the throw-
ing power, its use is hardly warranted, especially as nickel
solutions are so susceptible to any excess of colloids, the
concentrations of which are hard to determine or control.

θ - Hydrogen Peroxide. This is an oxidizing agent, the use of which has recently been recommended to prevent pitting. It causes a great decrease in throwing power, due to the fact that it requires a lower potential to reduce hydrogen peroxide than to deposit hydrogen or nickel; hence at low current densities the cathode efficiency is very low.

d - Sodium Sulphite. This compound was tried as a simple reducing agent. It improves throwing power at the higher current density, but produces dark and unsatisfactory deposits. It is included here simply because it suggests possible benefits in throwing power by the use of reducing agents.
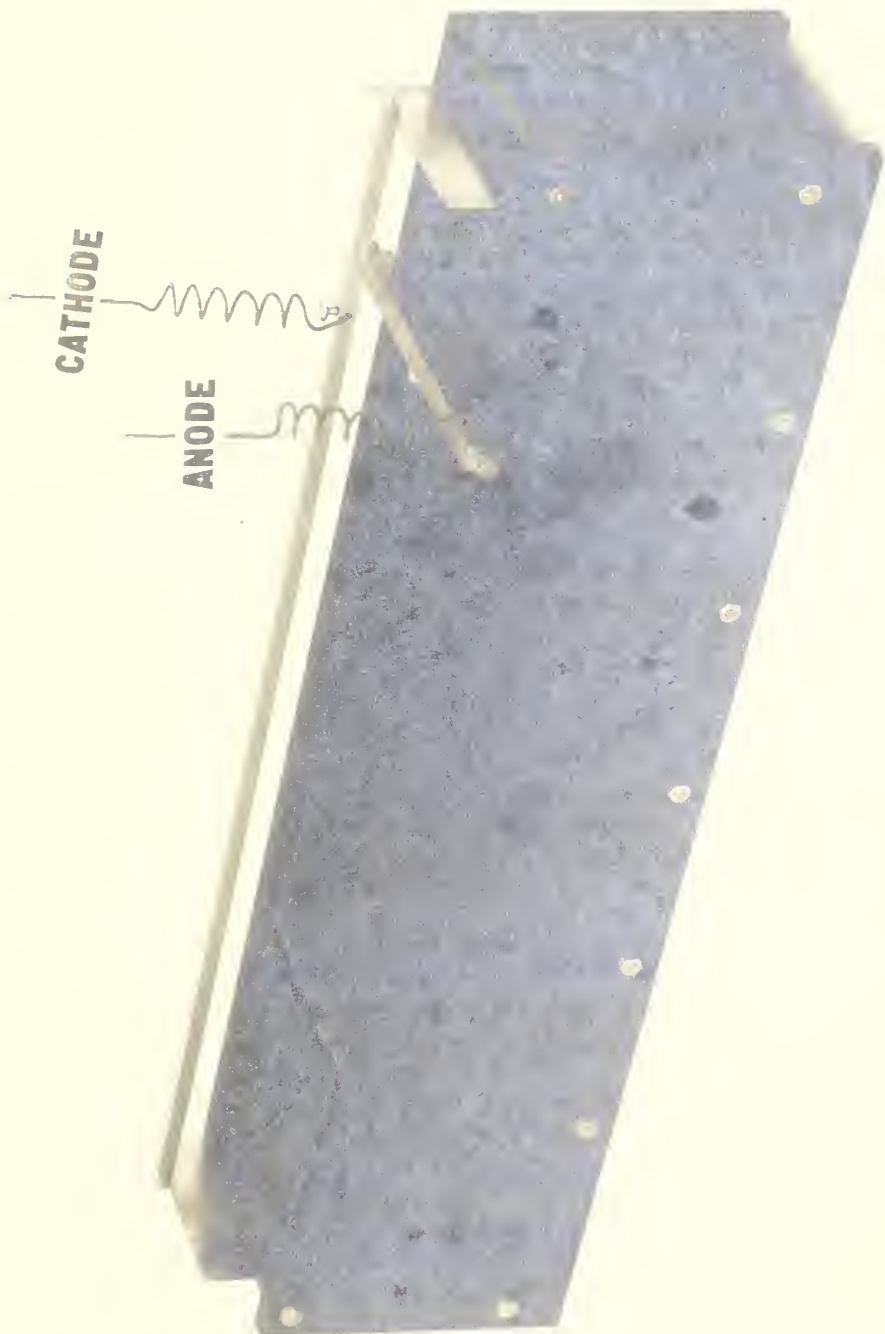
(8) Impurities. Previous work has shown that copper and zinc are the most detrimental metal impurities in nickel baths. Cadmium has often been used as a brightener, but its effects are so close to those of zinc that it may be included under this head. The effects of these metals upon the character of the deposits are more significant than those upon the throwing power.

In the amounts used, cadmium causes gray streaked deposits at low current densities, and bright deposits at higher current densities. In equivalent amounts, zinc gives good, bright deposits at both high and low current densities. Copper even in very small amounts causes dark spongy deposits at low current densities, but has little effect at the higher current densities. In general the injurious effects of all such metallic impurities will be most pronounced at low current densities, or when the solutions are heated. For such conditions nickel salts of greater purity than those formerly specified by this Bureau may be desirable.

5 - Conclusion

Because the throwing power is the resultant of three factors, each of which may vary with different metals, solutions or conditions, it is difficult to make any general rules for improving throwing power. It is possible however by a few simple measurements in the apparatus described to determine the probable direction and magnitude of the effect of any specified change in conditions, and thus be guided in their proper selection.

In any case, it should be remembered that an improvement in throwing power as here defined and measured, represents simply a more uniform distribution of metal, i.e. a lower consumption of metal to produce any specified minimum thickness of deposit on the article. Frequently however it is more economical to plate under conditions which yield a lower throwing power, e.g. at a higher current density, in order to save time and increase production, even though thereby a greater amount of metal is used to produce the desired result. The final choice of conditions must therefore be governed largely by expediency.

CATHODE

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