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NICKEL PLATING ON ZINC AND ZINC-BASE
DIE CASTINGS

This paper includes the principles and the conclusions of a research on this subject at the Bureau of Standards. Further details of the experiments were presented in a paper by M. R. Thompson at the April, 1935, meeting of the American Electrochemical Society, which will be published in Volume 47 of their Transactions.

1. General Principles

The fact that the nickel plating of zinc and of die-castings containing 85 to 95 per cent of zinc requires somewhat different conditions than the plating of brass or steel, is due to the greater tendency of the zinc to dissolve in the nickel solution. As is well known, if a piece of zinc is immersed in an ordinary nickel plating solution with no current flowing, it very quickly becomes coated with a black film. This film consists chiefly of metallic nickel that has been precipitated on the zinc in a finely divided spongy condition, by the zinc passing into solution and replacing the nickel. (In just the same way, when a piece of iron is hung in a copper sulphate solution, the iron dissolves and produces a deposit of copper "by immersion".)

The tendency for a metal to pass into solution, i.e. its "solution pressure" may be expressed in terms of the "single potential" of that metal in the solution. Thus, it may be shown that zinc tends to dissolve in a nickel solution with a potential of about -0.8 V. The negative sign of this potential is in accordance with the present usage of most technical societies. When a metal, such as zinc, has a strongly negative single potential, this indicates that it has a higher solution pressure and a greater tendency to dissolve than does a metal, such as copper, which has a positive single potential. In order to prevent the zinc from passing into solution and producing a spongy coating of nickel, to which the subsequent deposit will not adhere, it is necessary to apply to the zinc when it is hung in the nickel solution, a potential at least equal to that with which it tends to dissolve.

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As explained in the papers from the Bureau of Standards on "throwing power", whenever a metal is deposited, the concentration of the metal and metal ions always decreases in the film of solution next to the cathode. This decrease in concentration is naturally greater with a high than with a low current density, as the metal is taken out more rapidly at the higher current density. In consequence it requires a more negative potential at the cathode to deposit metal at a high than at a low current density. The difference between this potential at the cathode and that when no current is flowing is known as the "cathode polarization".

When an effort is made to plate a piece of zinc in an ordinary nickel plating solution at a low current density, it will be observed that the zinc turns dark on some parts, forming "black streaks", which indicates that, at the current density used on those parts of the cathode surface, the polarization is not sufficiently great to prevent the zinc from dissolving. If, however, as is customary in nickel plating on zinc, the current density is raised, a value will be reached at which no dark streaks are produced, which shows that then the cathode potential at all points is sufficiently negative to overcome the solution pressure of the zinc. It is comparatively easy to get from any nickel plating solution a good deposit of nickel on a flat sheet of zinc, on which the current distribution is nearly uniform, by sufficiently increasing the current density. For such purposes it is not unusual to apply, for a few minutes, a current density as high as 50 amperes per square foot, especially if the cathodes are moved.

If, however, the article to be plated is of irregular shape, as are most die castings and some objects made of sheet zinc, the current distribution will be far from uniform, and if the minimum current density required is 50 amp./sq.ft., that on some parts may be 100 or even 200 amp./sq.ft., and burnt deposits will be produced there. For such objects it is therefore desirable to employ a nickel solution in which the polarization is high, i.e. the required cathode potential (in this case -0.8 V) will be reached at a low current density, and in which there will then be less tendency for the near parts of the object to receive an excessive current density.

In this investigation the polarization of various nickel solutions was systematically studied, in order to select those in which zinc can be satisfactorily plated at the lowest current densities.

On general principles, it may be predicted that the nickel ion concentration in the cathode film during deposition may be decreased, and the polarization thereby increased by any of the following methods, all of which should therefore be beneficial for nickel plating on zinc.

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- 1 - Using a relatively dilute nickel solution.
- 2 - Using a nickel salt such as the sulphate, which forms fewer nickel ions than the chloride.
- 3 - Adding a salt with a common ion, e.g. sodium or magnesium sulphate, to a nickel sulphate solution.
- 4 - Forming "complex ions", for example by the addition of organic salts such as sodium citrate.
- 5 - By increasing the current density.
- 6 - By cooling the solution.
- 7 - By decreasing the "convection" of the solution (which is upward in still plating) along the face of the cathode, which movement tends to bring up fresh portions of the nickel solution. Convection may be hindered by (a) increasing the viscosity of the solution, (b) increasing the specific gravity of the solution, and (c) avoiding mechanical stirring.
- 8 - By the addition of colloids which "migrate" to the cathode and thus increase the polarization.

Among these possible methods, Nos. 4 and 5 have been most extensively applied in commercial practice, that is the addition of sodium citrate to the solution, or the application of a high current density in an ordinary solution. In many cases magnesium sulphate has been added to the solution in moderate amounts. The results of this study showed that sodium citrate has the greatest beneficial effect upon the polarization of any of the substances commonly used. If polarization were the only consideration, there would be no advantage in suggesting substitutes for sodium citrate. Actually, however, the sodium citrate solutions have certain disadvantages, such as relatively low throwing power and cathode efficiency, high cost, a tendency toward decomposition, and difficulty of control by analysis.

The most promising means of improvement appeared to be No. 3, i.e. the addition of some other sulphate in the highest possible concentration. Sodium and magnesium sulphates are the only common sulphates that can be used in high concentration in nickel solutions on account of solubility relations. Experiments showed that by adding a large amount of either of these salts a high polarization is produced and zinc can be plated at a relatively low current density from such solutions. Part of the increase in polarization is due

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to the fact that the addition of sulphates increases the density and viscosity of the solution and thus hinders convection (No. 7.). In general, nickel deposited at a relatively high polarization from this or any other type of solution is likely to be bright and hard.

In addition to this fundamental advantage of high polarization, the solutions with a high content of sodium or magnesium sulphate have very high conductivity and throwing power, they are easy to analyze and control, they do not readily decompose, and they are cheap. Either salt may be used, but the sodium sulphate produces the best conductivity and throwing power. Experiments in the laboratory and in commercial plants have shown that these "high-sulphate" solutions are well adapted for plating on zinc and zinc-base die castings. In addition, they are suitable for barrel plating of brass and steel, for which purpose the high conductivity and throwing power of the solutions, and the high luster of the deposits are especially advantageous. Any novelty in the recommendation of such solutions depends not upon the mere presence of the sodium or magnesium sulphate, which salts have been frequently used in nickel plating baths, but upon the relatively high concentration in which they are employed.

More extensive experience will be required to define the best conditions for applying this type of solution to each particular class of work. The following general range of conditions is suggested.

1 - Composition of Solution

	<u>N</u>	g/L	oz/gal
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (single salt)	0.5 to 1.0	70-140	9-19
Boric acid, H_3BO_3	0.25(M)	16	3.1
Ammonium chloride, NH_4Cl	0.35	13	1.7
Sodium sulphate (anhydrous), Na_2SO_4	1.5 to 3.0	107-213	14-28

Sodium sulphate may be obtained commercially either as the dry powder (Na_2SO_4) or as the crystallized salt, known as "Glauber's Salt", ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The former will usually be the more convenient to purchase on account of the saving in bulk and freight. If the crystallized salt is employed it is necessary to use 2.27 times as much as of the anhydrous salt. A fairly high grade of commercial sodium sulphate should be used, which does not contain excessive amounts of iron or of free acid or alkali, such as may be present in the lower grades of sodium sulphate.

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The solution with 3 N sodium sulphate, which contains 28 oz/gal of the anhydrous salt, or 65 oz/gal of the crystallized (Glauber's salt, is nearly saturated at ordinary temperature, and if the solution cools, some sodium sulphate will gradually crystallize out. Unless therefore the solutions are kept at a temperature above 60°F (15°C), it will not be possible to retain this maximum content of sodium sulphate in solution. As, however, the polarization, conductivity, and throwing power are all increased as the sodium sulphate content is increased, the latter should be kept as high as practicable under any existing conditions, in order to secure the maximum benefit from this type of bath.

2 - Conditions for Zinc and Die Castings

It is no more difficult to plate die castings than pure zinc if similar shapes are used. The greater difficulty often experienced in plating die castings is due to the fact that they are usually of very irregular shape. The following conditions are suggested for both zinc and die castings.

(a) A minimum average cathode current density from 15 to 20 amp./sq.ft. (1.5 to 2.0 amp./dm²) on simple shapes, and up to 35 amp./sq.ft. (4.0 amp./dm²) on complicated shapes.

(b) The bath voltage will usually be between 2 and 4 V, depending upon the composition and temperature of solution, the current density, the character of the anodes, and the electrode spacing. Owing to the higher conductivity of the solution it is not necessary to use as high a voltage to produce a given current density as in ordinary nickel solutions. Unless the current density is controlled, burnt deposits may be produced.

(c) The anode current density should be kept below 20 amp./sq.ft. (2 amp./dm²), by the use of a large area of clean anodes, preferably the 95-97 per cent cast anodes.

(d) The pH should be kept between 5.5 and 5.8.

(e) Moderate movement of the cathodes, as on moving rods, prevents burning on points of highest current density.

3 - Conditions for Barrel Plating Steel and Brass.

The lower suggested concentration of about 1.5 N sodium sulphate (14 oz/gal of Na₂SO₄ or 32 oz/gal of Na₂SO₄·10H₂O) has the advantage that the solution is less viscous, and

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hence there is less mechanical loss of solution when the work is removed. It is hard to define the current density in barrel plating owing to the irregular shapes and variable current distribution. In some cases the regular voltage for barrel plating (e.g. 6 to 8 V) has been applied, and owing to the greater conductivity the plating has been completed in a shorter time.

The use of a concentrated solution with high conductivity is likely to be new in the experience of most platers, and for specific purposes modifications may be required. In order to assist in such adjustments the Bureau of Standards will be glad to learn of the experiences of platers with this type of solution.

