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BEHAVIOR OF NICKEL ANODES

In connection with the general researches on nickel deposition at the Bureau of Standards, the behavior of nickel anodes was investigated. The purpose of this study was to survey the field, obtain reliable data upon the behavior of typical nickel anodes under definite conditions and point out the principal factors involved in their operation. A much more detailed study and more extensive plant observations will be required before the composition, preparation and properties of nickel anodes can be completely specified.

The details of the methods of study and of the numerical results obtained have been published[1]. In this Circular the results and conclusions of special interest to electroplaters are summarized.

To be entirely satisfactory, a nickel anode should corrode uniformly, with a low polarization and with a high anode current efficiency, and should not introduce any deleterious substances into the solution.

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[1] C. T. Thomas and W. Blum, Trans. Am. Electrochem. Soc., preprint, April, 1924.

If an anode does not corrode uniformly, small particles of metal are likely to become detached, and if they are carried over to the cathode they may cause roughness on the deposits. If large masses drop off, there is a waste of nickel.

If a metal such as copper is immersed in a solution of that same metal (e.g. copper sulphate), a certain voltage or potential difference exists between it and the solution. This potential difference is called its static or equilibrium potential. If now a potential even slightly greater than this is applied, the copper will dissolve. If, instead, a metal such as nickel is used, it requires a potential considerably greater than its equilibrium potential to cause it to dissolve; in other words it tends to become "passive". The excess potential is a measure of the anode polarization under those conditions. If this polarization is high, it requires a higher voltage to be applied to the bath to produce a certain current density or rate of deposition. The total voltage required under otherwise uniform conditions to produce with different anodes a certain current density upon them and upon the cathodes, is therefore a relative measure of the extent of the polarization with these respective anodes. If the polarization is high, oxygen may be discharged upon the anodes and cause "gassing" there.

The anode current efficiency is the proportion of the current which is used in dissolving metal from the anode. If in a certain case ten per cent of the current is used in the

liberation of oxygen, the remainder, i.e. ninety per cent, is consumed in dissolving nickel, in which case the anode efficiency is ninety per cent. Similarly the cathode efficiency is the proportion of the current used in the deposition of nickel, and the balance is employed in liberating hydrogen on the cathode.

If in a given nickel plating bath, the anode efficiency is exactly equal to the cathode efficiency, the bath will remain constant in composition and concentration (except for mechanical loss of solution which adheres to the cathodes when they are removed and which is replaced by water). If, however, the anode efficiency is not as high as the cathode efficiency, the nickel content of the bath decreases and at the same time the solution becomes more acid, i.e. the "pH" decreases, and poor deposits will result. If the anode efficiency is higher than that at the cathode, the metal content increases and the solution becomes less acid.

In order to measure the anode efficiencies of various kinds of nickel anodes, each was rotated separately in a small jar and the amount of nickel which dissolved when a given current was passed, was determined from the weight of nickel deposited on the cathode, and the change in nickel content of the solution. It is not possible to measure the anode efficiency with any accuracy from the loss in weight of the

anodes because small particles may drop off, or solution may be absorbed in the pores on the anode. In order to obtain reproducible results, the anode surfaces were kept clean. These results therefore represent the relative behavior of clean anodes and not of those upon which sludge has accumulated.

Three types of solutions were used in the experiments. The "single salt bath", No. 3, contained 19 oz/gal of nickel sulphate and 2.1 oz/gal of boric acid. No. 2, the "double salt solution" had the same total amount of metallic nickel (4 oz/gal) but contained 14 oz/gal of the single salt, 6.7 oz/gal of the double salt (nickel ammonium sulphate) and 2.1 oz/gal of boric acid. No. 1, the "chloride bath" contained 19 oz/gal of single salt, 2.1 oz/gal of boric acid, and 1.8 oz/gal of ammonium chloride.

The principal results obtained are summarized in the following table. Each anode was run in each solution at two current densities, viz. 4.6 and 14 amp./sq.ft., but only the results at the lower and more usual anode current density are tabulated. In general at higher current densities the anode efficiencies were lower than those listed. The bath potential V, given for only part of the anodes, represents that required to produce this current density in the particular apparatus used. The figures represent therefore the relative and not the actual potentials that may be required in any other baths in actual commercial use, and are included merely to indicate the relative extent of the polarization under different conditions.

Behavior of Nickel Anodes

Anode No.	Description	Solution Composition[1] %		1-Chloride		2-Double Salt		3-Single Salt	
		C		An. Ef. %	V	An. Ef. %	V	An. Ef. %	V
1	Electrolytic			100	1.30	53	2.45	36	2.50
2	Rolled	0.1		100	1.25	68	2.40	68	2.55
3	Oxidized		0.5 NiO	100	0.90	90	2.35	73	2.50
4	Sand cast	0.1		99		80		84	
5	Chill cast	0.4		100	1.20	91	2.35	91	2.40
6	Sand cast	0.4		99	1.25	89	2.35	91	2.35
7	Chill cast	1.5		99		94		94	
8	Sand cast	1.5		99	1.20	96	2.25	95	2.25
9	" "	0.5	0.15 S	98		93		95	
10	" "	0.5	" +Mg	98		78		77	
11	" "	1.5	0.15 S	98		94		95	
12	" "	1.5	" +Mg	99		90		92	
13	" "	0.1	1.5 Fe	98		78		80	
14	" "	1.5	"	99	1.20	96	2.10	96	2.25
15	" "	1.0	6.0 Fe	99		93		93	
16	" "	1.5	1.5 Si	95		94		94	
17	" "	1.5	1.0 Cu	100		100		95	
18	" "	1.5	1.0 Sn	99		83		89	
19	A Shot[2]	0.1		98		83		89	
20	M Shot[3]	0.06		99		80		60	

[1] C = carbon, NiO = nickel oxide, S = sulphur, Mg = magnesium, Fe = iron, Si = silicon, Cu = copper, Sn = tin.

[2] Chilled shot, made by pouring molten nickel into water.

[3] Spherical shot, made by the Mond process.

Conclusions

From the results in Table 1 and other data, the following conclusions may be drawn regarding the behavior of these anodes under the conditions used in these tests.

A - Composition of Solution. In solutions such as No. 1 containing an appreciable amount of a chloride, e.g. sodium chloride or ammonium chloride, the anode efficiency of all the anodes is very close to 100 per cent. A few experiments with solutions containing fluoride instead of chloride, showed that fluorides do not increase the anode efficiency appreciably above that in the plain single or double salt solutions.

In solutions containing chlorides, such as are now generally used, the choice of anodes will therefore depend principally upon their purity and the uniformity of their corrosion.

B - Composition of Anodes. The anodes listed in the table may be divided roughly into two classes, viz (a) those consisting of nearly pure nickel, such as the electrolytic, rolled, shot and oxidized nickel; and (b) those containing appreciable amounts of other elements, such as carbon, iron, silicon and tin which are often added intentionally, chiefly for the purpose of lowering the melting point and facilitating casting.

All forms of nearly pure nickel have a relatively low anode efficiency in solutions which do not contain chlorides, but a high efficiency if chlorides are present. The effects of various additions may be summarized as follows.

Carbon - Carbon is the most common addition to cast nickel anodes, which usually contain from 0.5 to 2.0 per cent of carbon. Its chief effect upon the behavior is to decrease the passivity and polarization and to increase the anode efficiency in solutions which do not contain chlorides. If more than about 0.5 per cent of carbon is present, it crystallizes out as graphite, the particles of which accelerate the corrosion of the nickel because the graphite is less readily attacked than the nickel. The more graphite is present in a finely divided condition, the more uniformly does the anode corrode.

Nickel Oxide - Nickel which is melted with no addition of carbon, may contain a small amount of nickel oxide (No. 3). This substance separates on cooling, and as it is less soluble than nickel it also aids in the corrosion of the nickel.

Nickel Sulphide - If from the gas, oil or coal used in melting the nickel, any appreciable amount of sulphur is taken up, it forms nickel sulphide which separates along the grain boundaries of the nickel. As however nickel sulphide is more readily attacked than nickel, it dissolves out first and allows the particles of nickel to drop out. The presence of an amount of sulphur above 0.10 per cent in nickel anodes is therefore deleterious, especially if the carbon content is below 1 per cent. This effect of sulphur is not overcome by adding magnesium to the molten nickel.

Iron - Moderate amounts of iron in nickel anodes which contain sufficient carbon, tend to produce more uniform corrosion.

It has been shown that iron is not necessarily detrimental in nickel solutions. As, however, it is seldom beneficial and as it does cause an accumulation of sludge upon the anodes and in the solutions, there is no justification for adding it to the anodes, as was done with the 90-92 per cent anodes which were formerly in general use.

Copper - Small amounts of copper have been shown to be very harmful in nickel solutions, and therefore no copper should be added to nickel anodes. If, as an accidental impurity, the anodes contain not over 0.25 per cent of copper, and they are dissolving readily, i.e. are not passive, most of this copper will stay on the anodes and not contaminate the solution or the deposit.

Silicon and Tin - Both of these elements may be added to nickel to aid in the casting. They have no beneficial effect on anode behavior, and they pass into the sludge and not into the deposit. To the extent that they increase the sludge formation upon the anodes or in the solution, they are objectionable.

C - Type of Anodes. As all kinds of nickel have a high anode efficiency in solutions containing chlorides, differences in behavior relate chiefly to the uniformity of corrosion. A greater tendency toward detachment of small particles was observed with the electrolytic, rolled, shot and chilled cast anodes than with the high carbon sand cast anodes. It is tentatively suggested that cast nickel anodes should be

sand cast and should contain not less than 95 per cent of nickel and 1.25 per cent of carbon, and not more than 0.1 per cent of sulphur or 0.25 per cent of copper. Amounts up to 1 per cent each of iron, tin, and silicon may be permitted, but are not recommended.

Potentials - The most significant conclusion from the bath potentials listed in the table is that to produce a given current density in the chloride solutions approximately one volt less is required than in baths containing no chlorides. This illustrates the great advantage of chlorides in reducing the passivity and polarization of nickel anodes.

The difference in voltage between different anodes in the chloride solution is usually only 0.1 to 0.3 volt. Such differences have no economic significance in themselves. They illustrate, however, the behavior of two kinds of anodes, e.g. electrolytic and cast, if they are hung simultaneously in the same bath or in similar baths connected in parallel with the same voltage applied to each. In such cases most of the current will pass to the cast anode, i.e. the one which will dissolve at the lowest potential and in consequence more metal will be dissolved from it than from the electrolytic anode. This is no proof however that the electrolytic anode would not corrode with a high anode efficiency if no other kind of anode was present in the same bath, or in parallel baths.

As previously indicated, more extended observations upon the commercial preparation and use of nickel anodes will be

needed before their behavior can be thoroughly understood. It is hoped that such study and observation will be stimulated by the publication of the results of these laboratory experiments.