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CONDUCTIVITY OF NICKEL SOLUTIONS

This investigation was conducted as a part of the general study of nickel deposition in progress at the Bureau of Standards. The conductivity of nickel solutions such as are used in electroplating and electrotyping is important because it may affect the power cost, the throwing power and the character of the deposits. The conductivities of nickel sulphate solutions containing such substances as are commonly added to nickel baths were therefore determined. The details of the methods used in the investigation have been described in a recently published article[1]. The

[1] L. D. Hammond - "Conductivity of Nickel Depositing Solutions", Trans. Am. Electrochem. Soc., Vol. 45, (preprint) April 1924.

results of interest to electroplaters may be summarized as follows:

To avoid confusion it is desirable to distinguish clearly between the following terms, viz. resistance, resistivity, conductance and conductivity. The <u>resistance</u> of any bath containing two electrodes is expressed in <u>ohms</u>, and (if we disregard polarization) it is equal to the applied voltage

divided by the current in amperes. Thus if when a potential of 3 volts is applied to a certain bath, a current of 300 amperes flows, the resistance of the bath is equal to 3/300 = 1/100 or 0.01 ohms.

The resistivity of the solution in the vessel is the resistance of a definite portion of that solution contained between two electrodes of a definite size and at a definite distance from each other. The customary unit of resistivity is that of a "centimeter cube" of solution having a resistance of one ohm between two electrodes each 1 cm square and one centimeter apart. This unit is called the ohm-centimeter, and the resistivities so expressed are often referred to as "ohms per centimeter cube". It is possible to express and compare the resistivities in terms of the "inch cube", the resistivity of which is equal to 0.39 times that of the "centimeter cube". As, however, we are usually concerned with relative and not actual values, there is no advantage in converting the metric to the English units.

The conductance is the reverse or reciprocal of resistance, and conductivity is the reciprocal of resistivity. Thus if the resistance of a certain bath is 0.01 ohm, its conductance is 100 "reciprocal ohms". Similarly if the resistivity of a certain solution is 25 ohm-centimeters, its conductivity is 1/25 or 0.04 reciprocal ohm-centimeters.

In the usual determination of electrical conductivity, it is customary to measure the resistance, in ohms, of a

vessel or "cell" filled with the solution. The electrodes are of platinum, coated with spongy platinum or "platinum black", and an alternating current is used in order to eliminate the effects of "polarization", such as may be caused by changes in the concentration of the solution near the electrodes during electrolysis with a direct current. The resistivity of the solution is calculated from the resistance of the cell when filled with a solution of known resistivity.

The numerical results in this paper are given in terms of resistivity in ohm-centimeters. In considering these data, it is important to remember that a decrease in resistivity corresponds to an increase in conductivity.

Table I

Resistivity of Nickel Sulphate Solutions

at 25°C (77°F)

Concentration of $NiSO_4.7H_2O$			Resistivity ohm-cm
N	g/L	oz/gal	
0.5	70	9	53.0
1	140	19	34.4
2	281	37	22.2
3	421	56	19.0
4	562	75	18.3

From Table 1, it may be seen that increasing the concentration of nickel sulphate from 9 to 37 oz/gal makes a decided increase in conductivity, but beyond that point the improvement is not sufficient to warrant the increased cost of stronger solutions and the consequently greater loss of material in the solution which adheres to the work.

Table 2

Resistivity of Normal Nickel Sulphate Solution (140 g/L or 19 oz/gal) containing added compounds.
At 25°C (77°F)

Added Compound Name	Formula	Concentration N	g/L	oz/gal	Resistivity ohm-cm
Sodium sulphate	Na_2SO_4	0.1	7	0.9	29.4
		0.2	14	1.9	26.2
		0.5	36	4.8	20.0
		1.0	71	9.5	15.0
Potassium sulphate	K_2SO_4	0.1	9	1.2	28.1
		0.2	17	2.3	24.2
Ammonium sulphate	$(NH4)_2SO_4$	0.1	7	0.9	28.0
		0.2	13	1.7	24.0
		0.4	26	3.5	18.8
Magnesium sulphate	$MgSO_4.7H_2O$	0.1	12	1.6	31.5
		0.2	25	3.3	29.4
		0.5	62	8.3	25.3
		1.0	123	16.5	21.1
Sodium chloride	NaCl	0.1	6	0.8	27.0
		0.2	12	1.6	22.5
		0.5	29	3.9	15.4
		1.0	58	7.8	10.5
Ammonium chloride	NH_4Cl	0.1	5	6.7	26.0
		0.2	11	1.5	21.1
		0.4	21	2.8	15.3
Nickel chloride[1]	$NiCl_2.6H_2O$	0.2	24	3.2	27.2
		0.5	59	7.9	20.5
Sodium fluoride	NaF	0.1	4	0.5	28.8
		0.2	8	1.1	25.5
		M			
Boric acid	H_3BO_3	0.1	6	0.8	33.9
		0.2	12	1.6	34.1
		0.5	31	4.1	35.0

[1] In the solutions containing nickel chloride the nickel sulphate concentration was correspondingly decreased so that the total nickel concentration was always normal, as in the other solutions.

From Table 2 and Fig. 1 (Insert Fig. 1) it may be seen that the resistivity of normal nickel sulphate solution (34.4 ohm-cm) is decreased by the addition of each of the compounds listed except boric acid, which has a practically negligible effect. Of the four sulphates tested, equivalent additions of the magnesium sulphate have the least effect, and in small concentrations ammonium sulphate has the largest effect. The possible concentration of ammonium sulphate is, however, limited by the low solubility of the nickel ammonium sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$ (the common "double nickel salt").

Similarly low concentrations of ammonium chloride produce a greater increase in conductivity than do equivalent amounts of sodium chloride. Owing to the limited solubility of the ammonium chloride in the nickel sulphate solution, a higher conductivity can be produced by the addition of sodium chloride than with any of the other salts tested. The indications are, however, that the ammonium chloride has a more beneficial effect upon the character of the deposit than has the sodium chloride.

Table 3

RESISTIVITIES OF NORMAL SOLUTIONS AT 25°C (77°F)

Name	Formula	Concentration g/L	Concentration oz/gal	Resistivity Ohm-cm
Hydrochloric acid	HCl	36.5	4.9	3.07
Sulphuric acid	H_2SO_4	49	6.6	4.8
Acetic acid	$HC_2H_3O_2$	60	8.0	670
Boric acid	H_3BO_3(M)	62	8.3	70000
Potassium hydroxide	KOH	56	7.5	5.7
Potassium chloride	KCl	74.5	10.0	8.9
Potassium cyanide	KCN	65	8.7	8.2
Sodium hydroxide	$NaOH$	40	5.4	5.7
Sodium chloride	$NaCl$	58.5	7.8	11.6
Sodium fluoride	NaF	42	5.6	18.5
Sodium sulphate	Na_2SO_4	71	9.5	16.8
Sodium carbonate	Na_2CO_3	53	7.1	18.7
Sodium phosphate	$Na_2HPO_4 \cdot 12H_2O$	119	16.0	31.5
Ammonium hydroxide	NH_4OH	35	4.7	970
Ammonium chloride	NH_4Cl	53.5	7.2	9.0
Ammonium sulphate	$(NH_4)_2SO_4$	61	8.2	12.9
Calcium chloride	$CaCl_2$	56	7.5	13.2
Magnesium sulphate	$MgSO_4 \cdot 7H_2O$	123	16.5	29.9
Copper sulphate	$CuSO_4 \cdot 5H_2O$	125	16.7	34.1
Zinc sulphate	$ZnSO_4$ $7H_2O$	144	19.3	32.1
Zinc chloride	$ZnCl_2$	68	9.1	13.4
Cadmium sulphate	$CdSO_4$	104	13.9	38.
Cadmium chloride	$CdCl_2$	92	12.3	40
Ferrous chloride	$FeCl_2 \cdot 4H_2O$	99	13.2	14.5
Ferrous sulphate	$FeSO_4 \cdot 7H_2O$	139	18.6	31.6
Nickel sulphate	$NiSO_4 \cdot 7H_2O$	140	18.8	34.4
Nickel chloride	$NiCl_2 \cdot 6H_2O$	119	16.0	14.1
Cobalt sulphate	$CoSO_4 \cdot 7H_2O$	141	18.9	34.1
Cobalt chloride	$CoCl_2 \cdot 6H_2O$	119	16.0	14.5

In order to compare the resistivities of the nickel solutions with those of other solutions such as may be used in plating operations, Table 3 has been compiled. From this table it may be seen that in normal or chemically equivalent solutions, the strong acids and alkalis have the lowest resistivity or highest conductivity. The sulphates of the "heavy" metals, such as iron, nickel, cobalt and zinc have relatively high resistivities, which can be reduced by the addition of better conducting salts, such as the chlorides and sulphates of sodium, potassium and ammonium. When, as in copper sulphate solutions, a high concentration of sulphuric acid is permissible, the conductivity may be thereby greatly increased. With nickel solutions, however, which must be kept nearly neutral, it is not practicable to increase the conductivity to approach that of the acid copper bath.

Resistivity of Normal Nickel Sulfate Solutions Containing Added Compounds at 25°C $N-NiSO_4 = 34.4\ \Omega\text{-cm.}$