THE RELATION OF ELECTROPLATING TO ELECTROLYTIC ANALYSIS

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The ideal solution for the plater is one from which he can precipitate the metal quantitatively in as nearly an amorphous form as possible and in which the anode will dissolve quantitatively. The two requisites then are a very finely crystalline deposit at the cathode and a practically constant composition of the solution. The analyst does not require so finely crystalline a deposit at the cathode, though he is glad to get it. He uses an insoluble anode and consequently is not necessarily limited in his choice of an acid radical. He does not get and does not expect to get one hundred percent current efficiency at the cathode. In these three respects he demands less than the plater. On the other hand, the analyst must get a good deposit from a solution of changing concentration down to the point at which no metal remains in solution. He must not only get the last trace of the metal out of the solution but he must precipitate it in a weighable adherent form while there is a copious evolution of hydrogen going on. In this respect the analyst's requirements are much more rigid than those of the plater. Since the analyst has to weigh the deposit, he cannot improve its quality by adding a colloid to the solution as may be done by the plater.

If a plating bath will give a good deposit for any and all concentrations of the metal, it may be used as a solution in which electrolytic analysis is carried on. If a solution for electrolytic analysis gives a sufficiently fine-grained deposit and if the anode will dissolve practically quantitatively in it, such a solution may be used as a plating bath. We should therefore expect to find that under certain circumstances the same solutions are used both for electrolytic analysis and for plating. We should further expect that in some cases the two sets of solutions will differ and that the reason for the difference will lie in the non-fulfilment of one or more of the

requirements just specified. The object of this paper is to show in how far actual practice coincides with the theoretical conclusions.

In a previous paper¹ I have shown that the essential thing in securing a good metallic deposit is to prevent the precipitation of a salt of the metal with the metal. Whenever the oxide, hydroxide, cyanide or other salt separates on the cathode we invariably get a spongy deposit. Consequently any useful additions to the plating bath, which are not for the purpose of increasing the fineness of the crystals or of regulating the acidity, must consist of substances which dissolve the oxide, hydroxide, cyanide, or whatever the disturbing salt may be. In the deposition of zinc the addition of sulphuric acid, potash, ammonium chloride, ammonium sulphate, aluminum sulphate, potassium cyanide or acid potassium oxalate has been recommended. The first four dissolve zinc hydroxide and the potassium cyanide dissolves zinc cyanide. Of the substances added to nickel baths, sulphuric acid, ammonia and ammonium salts dissolve nickel hydroxide and potassium cyanide dissolves the cyanide. Sodium bicarbonate and boric acid serve to regulate the acidity. In lead baths acetic acid, potash, sodium nitrate and fluosilicic acid dissolve lead hydroxide though by no means equally well or equally rapidly. Sulphuric acid, potash, sodium phosphate, and ammonium oxalate dissolve stannous and stannic acids while ammonium sulphide dissolves the sulphide. Sulphuric acid, ammonia, alkaline tartrate, and ammonium oxalate dissolve cuprous oxide while potassium cyanide dissolves the cyanide. Nitric acid and ammonia dissolve freshly precipitated silver oxide; ammonia dissolves silver chloride; potassium cyanide dissolves silver cyanide; while silver iodide is soluble in potassium iodide. Gold cyanide is soluble in potassium cyanide and gold sulphide in sodium sulphide. The oxides of gold are soluble in bisulphide, thiosulphate and sulphocyanate solutions. A phosphate solution also has a solvent action.²

¹ Jour. Phys. Chem., 9, 277 (1905).

² Cf. Becquerel: Phil. Mag. [5] 8, 136 (1879).

While we cannot at present predict whether one metal will give larger crystals than another when precipitated electrolytically from the sulphate solution for instance, we can tell how the size of the crystals will vary for any given metal with varying conditions of precipitation. In the paper already referred to I have shown that we may consider the electrolytic precipitation of a crystalline metal as governed by the general laws of crystallization and that the conditions favoring a nearly amorphous precipitate are high potential difference between metal and solution, high current density, low temperature, and presence of a colloid which migrates to the cathode.¹ Since platers do not stir their solutions to any extent, high current densities are not possible, and it is necessary to use solutions that give a finely crystalline deposit at moderate current densities. By using a dilute solution one can get smaller crystals than with a concentrated solution but as the conductivity of a dilute solution is low, the tendency to tree is greater and there is no real gain. If we take into account the danger of impoverishment at the cathode, there is a great disadvantage in the use of dilute solutions and, as a matter of fact, they are not used. We can get a greater difference of potential between metal and solution without any corresponding decrease of conductivity by using a complex salt of the metal to be deposited. If we take potassium silver cyanide for instance we may have a high absolute concentration of silver together with a low concentration of silver as ion. The conductivity of the solution is almost infinitely higher than that of a silver nitrate solution, having the same concentration of silver as ion and the danger of treeing is correspondingly reduced. As a matter of fact we do get a beautiful deposit of silver from a cyanide solution while that from a nitrate solution is so coarsely crystalline under ordinary circumstances as to be worthless to the plater. Another well-known advantage of using a complex salt is the way in which it minimizes the danger of spontaneous precipitation in the plating of baser metals. While the use of colloids is not a regular thing among platers we know that the

¹ Cf. Müller and Bahntje: *Zeit. Elektrochemie*, 12, 317 (1906).

addition of a little gelatine has a wonderful effect with zinc, lead, tin, copper and silver.

In plating with copper, practically only two solutions are used, a cyanide solution and a solution of copper sulphate acidified with sulphuric acid. The deposit from the cyanide solution is finer than that from the sulphate solution; but as the deposit from the latter is fine enough, the sulphate solution is used almost exclusively. The cyanide solution is useful as a striking bath; but it is more expensive, more dangerous, and has a higher resistance. An alkaline tartrate solution has also been recommended for plating but has not come into general use.

Copper can be precipitated electrolytically from almost any solution. It has been precipitated quantitatively from acidified sulphate, acidified ammonium oxalate, acidified phosphate, ammoniacal ammonium nitrate, cyanide, and other solutions. Most analyses are made in an acidified copper sulphate solution, while the cyanide is used when one starts with copper sulphide. The two plating solutions are therefore identical in nature with two of the solutions used for electrolytic analysis. The differences in composition are natural ones when we keep in mind the differences in the ends to be obtained. In the plating solution the sulphuric acid serves the double purpose of preventing the precipitation of cuprous oxide and of increasing the conductivity of the solution. There is therefore no object in keeping the sulphuric acid content down to a minimum and it may run anywhere from four percent to twelve percent or even more. On the other hand, with so much free acid it would be difficult to get the last traces of copper out, and the solution for electrolytic analysis contains only a little free acid at the start. This free acid is usually nitric acid because there is danger of reducing sulphuric acid to hydrogen sulphide during the last portion of the run when one is really electrolyzing a sulphuric acid solution with a copper cathode. The nitric acid prevents this reduction, being itself reduced to ammonia. In the plating bath there is always plenty of copper sulphate in solution and consequently there is no danger of any reduction of the sulphuric acid.

The only difference between the cyanide plating bath and the cyanide analytical bath is that the initial ratio of cyanide to copper may be lower in the latter because the anode does not dissolve. It is not necessary that the ratio of cyanide to copper should be lower in the analytical solution than in the plating bath because the cyanide is oxidized at the platinum anode and can therefore be brought to any desired concentration by prolonging the electrolysis sufficiently. It is pretty wasteful, however, to add more cyanide than is necessary merely for the sake of decomposing it afterwards. In any case most of the cyanide must be decomposed if all the copper is to be precipitated¹ at 20°.

Doubtless many of the other analytical baths could be used for copper plating. Curry² has shown that a copper anode dissolves quantitatively in an acidified ammonium oxalate bath. Since such a bath has apparently no especial advantage as a plating bath over the two standard ones,³ there is no reason why it should come into use. The same reasoning applies to the acidified phosphate bath, while in the ammoniacal nitrate solution it is doubtful whether the current efficiency at the cathode approximates one hundred percent.

The cyanide solution is the only one in use in plating silver, though an iodide solution has been recommended highly. A good deposit can be obtained from the cyanide for all concentrations of silver and consequently the cyanide solution can be and is used in the electrolytic determination of silver. For analytical purposes the nitrate solution is also used, but the deposit is so coarsely crystalline that it is entirely unsuitable for plating purposes. A good plating deposit can be obtained from the nitrate solution by using high current densities and a rapidly rotating cathode,⁴ but this would not be practicable in commercial practice. A good deposit can

¹ Cf. Root: *Jour. Phys. Chem.*, 7, 461 (1903).

² *Jour. Phys. Chem.*, 10, 489 (1906).

³ It may be useful as a bronzing bath. Cf. Curry: *Jour. Phys. Chem.*, 10, 515 (1906).

⁴ Snowdon: *Jour. Phys. Chem.*, 9, 392 (1905).

also be obtained by adding gelatine to the nitrate solution. This is in actual use at the Philadelphia Mint in the electrolytic refining of silver by the Moebius process, but I do not know of its use in any plating establishment.

The plating baths for gold all contain cyanide, ferrocyanide, thiocyanate, thiosulphate or bisulphite. Of these, the cyanide bath is by far the most important. For analytical purposes the solutions in use contain potassium cyanide, potassium sulphocyanate and sodium sulphide respectively. I cannot find any record of a sulphide bath having been used for plating purposes, and it seems not improbable that a gold anode does not dissolve readily in such a solution. There is also a possible danger of forming a film of sulphide on the surface of the metal which is to be plated. Either of these would prevent the use of the sulphide bath for plating purposes. Special experiments are necessary to show whether these suggested objections are real or imaginary ones.

While on the subject of gold-plating there is a passage from McMillan's book which I should like to quote:¹

"A current which is too strong will, of course, deposit the gold as a black powder; but within the limits between which coherent and adhesive deposits are yielded, a stronger current produces a deeper coloured coating than a weak current. Hence, speaking generally, any influence which tends to increase the current-volume gives rise to a metal possessing a warmer hue. A feeble current, a small anode, and a cold solution, alike, give, pale yellow deposits; but a stronger battery, an increase of anode-surface (and hence less resistance), or warming the liquid, increase the current-strength, and a deeper yellow tone prevails. Motion imparted to the pieces also causes the production of a lighter colour."

No explanation was offered by McMillan, but it all becomes clear if we may postulate that gold has a warmer color the more finely crystalline it is. Higher current density would give smaller crystals and therefore a warmer color. Stirring

¹ McMillan: "A Treatise on Electrometallurgy," 2nd edition, 225.

the solution prevents impoverishment at the cathode and therefore keeps the potential difference down somewhat, thereby causing an increase in the size of the crystals and the consequent production of a lighter color. Raising the temperature would in itself increase the size of the crystals, but the increase in the current density may more than neutralize that tendency. The hypothesis could be tested by examining the samples of gold-plating under the microscope or by making runs with the same current density at two different temperatures and noting the differences in shade, if any. In support of this hypothesis is the fact¹ that metallic gold can be precipitated in a dilute liquid in so fine a state that it remains suspended, and under these circumstances it appears by reflected light, of a purple-red, whilst by transmitted light it assumes a blue color."

While not strictly germane to the subject of this paper, there is a quotation from Roseleur² which calls attention to a theoretical difficulty which has now disappeared. "It is a remarkable phenomenon that solutions of cyanides, even without the action of the electric current, rapidly dissolve in the cold, or at a moderate temperature, all the metals, except platinum, and that at the boiling-point they have scarcely any action upon the metals." The explanation of this is that potassium cyanide forms complex salts with the cyanides of the metals at ordinary temperatures and that these complex salts break down more and more with rising temperature. Root³ found that, in fourth-normal cyanide solution and 0.2 g metal per 200 cc solution, cadmium precipitates before copper at 20° while the reverse is the case at 60°. With double-normal potassium cyanide solution and 0.2 g metal per 200 cc solution, mercury and cadmium precipitate before silver at 20° and silver before mercury and cadmium at 60°.

The plating baths for nickel consist of nickel sulphate and ammonium sulphate in varying proportions with and without

¹ Roscoe and Schorlemmer: "Treatise on Chemistry," 2nd, 373.

² Watt and Philip: "Electro-Plating and Electro-Refining, 182."

³ Jour. Phys. Chem., 7, 461 (1903). Cf. also Foerster: Zeit. Elektrochemie, 13, 561 (1907).

additions of ammonia, citrate, tartrate, etc. Pfanhauser¹ recommends the use of sodium salts instead of ammonium salts. Since nickel anodes do not dissolve readily in sulphate solutions, pure anodes are practically never used commercially. An alloy of iron and nickel is used² instead with the corresponding disadvantage that the plating deposit contains iron also. Electroplating with nickel is, therefore, not strictly comparable with electroplating with copper, silver or gold, and would come under the same category as the electrodeposition of brass, except that apparently no one knows or cares how much iron is precipitated with the nickel.³ If the solution contained a chloride, the whole difficulty would disappear.

Nickel is determined electrolytically in an ammoniacal sulphate solution, in ammonium oxalate solution, in cyanide solution, and in an ammoniacal phosphate solution. Nickel cannot be determined electrolytically in a straight ammonium sulphate solution because the solution soon becomes so acid that it is impossible to get any more nickel to precipitate. An oxalate solution is useless for plating, because a nickel anode does not corrode to any extent in it. As nickel cannot be precipitated at all from a solution containing more than the merest excess of cyanide, the cyanide solution is not used as a plating bath. Plating could probably be carried on in a phosphate bath, but it is not known that there would be any advantage over a sulphate bath.

The plating baths for tin consist of an alkaline stannate solution and a so-called pyrophosphate solution. Since sodium pyrophosphate changes gradually in solution to disodium phosphate, it seems doubtful whether the advantages claimed for a "pyrophosphate" bath are really due to sodium pyrophosphate. Until this question is settled experimentally, it seems wiser not to consider this solution. Tin is determined analytically in ammonium oxalate solution and in ammonium

¹ *Die Galvanoplastik*, 42.

² Cf. *Brass World*, 1906, 317.

³ This state of things is gradually changing. Cf. Calhane and Gammage: *Jour. Am. Chem. Soc.*, 29, 1268 (1907).

sulphide solution. There is no apparent reason why an acidified ammonium oxalate solution should not be used for plating purposes.¹ With regard to the sulphide solutions, the same question arises as with the sodium gold sulphide solution. No method is given in Smith's "Electro-Analysis" for the determination of tin in alkaline solutions, but I see no reason why such a method should not be worked out if anybody cared to experiment with it.

Plating baths for zinc consist of sulphate, cyanide, zincate, and chloride plus ammonium chloride. The sulphate and the chloride solutions yield a more coarsely crystalline deposit than do the zincate and cyanide solutions. As zinc is deposited rather as a protective covering than as a thing of beauty, a coarseness of crystalline structure is not a serious drawback though it unquestionably is not an advantage. Zinc is determined electrolytically in sulphate, acetate, citrate, cyanide, zincate and oxalate solutions. The zincate, sulphate, and cyanide solutions occur in both sets, the ammonium acetate solution is valuable only because of the solution not becoming strongly acid, and an acidified oxalate solution could undoubtedly be used as a plating bath.

The chloride-plating bath does not find its analogue among the analytical solutions and that brings us to what is for the moment a fundamental difference between the two kinds of solutions. Plating baths often contain chlorides; solutions for electrolytic analysis practically never did until recently. When a soluble anode is used, as in plating, there is no danger of free chlorine. With a platinum anode there is always danger of the solution containing free chlorine, hypochlorous acid, or hypochlorites, any one of which would cause trouble at the cathode. There is also a possibility of the platinum anode being attacked if the current density is high.² Except perhaps in the case of copper the objection is not to chlorides in themselves but to their decomposition products. If one were to add something to the solution, which would act

¹ Cf. Curry: *Jour. Phys. Chem.*, **10**, 489 (1906).

² E. F. Smith: "Electro-Analysis," 4th Edition, 89.

as a depolarizer for chlorine and prevent its being set free, the disturbing effect would be eliminated. This has been done at the University of Pennsylvania in a very ingenious manner. A layer of toluene or xylene is placed above the solution and absorbs the halogen completely.¹ The general principle has been applied in an even more ingenious way in special cases,¹ also at the University of Pennsylvania. By using a silver anode the halogen is changed to the corresponding silver halide and can be weighed directly. This method of eliminating a difficulty gives a quantitative electrolytic determination of the halogens.

The general results of this paper may be summed up as follows:

(1) Cyanide and sulphate baths are used both for electroplating with copper and for the electrolytic determination of copper. The acid ammonium oxalate and acid phosphate baths are used only for the electrolytic determination of copper but could be used as plating solutions. That the cyanide solution can be used for the electrolytic determination of copper is made possible by the electrolytic oxidation of the cyanide at the platinum anode.

(2) Cyanide baths are used both for electroplating with silver and for the electrolytic determination of silver. A nitrate solution is used for the electrolytic determination only, since the deposited silver is too coarsely crystalline for plating purposes unless a very high current be used or a colloid be added.

(3) Cyanide and sulphocyanate are used both for electroplating with gold and for the electrolytic determination of gold. Ferrocyanide solutions are used as plating baths, but present no advantage over the cyanide and sulphocyanate from an analytical point of view, and therefore have not been studied with this in mind. Sodium gold sulphide solutions are used for electrolytic determinations, but the possibility of their forming a sulphide film of baser metal seems to make them objectionable for plating baths.

¹ E. F. Smith: "Electro-Analysis," 4th Edition, 285.

(4) Nickel can be determined electrolytically in an ammoniacal sulphate solution, an ammonium oxalate solution, a cyanide solution, or an ammoniacal phosphate solution. Only a sulphate solution is used for plating. An oxalate solution would not corrode the anode while a cyanide solution would be too difficult to regulate. A phosphate solution could probably be used for plating.

(5) There is no relation between the plating and the analytical solutions with tin, plating being done with an alkaline stannate solution while ammonium oxalate and ammonium sulphide solutions are used for electrolytic analysis. It is possible that plating could be done with an oxalate solution and that tin could be determined analytically in an alkaline solution.

(6) Cyanide, sulphate, zincate, and chloride solutions are used in plating with zinc. The first three are also used for electrolytic analysis. Zinc is also determined electrolytically in an oxalate solution, which would probably work well as a plating bath.

(7) Chlorides are not permissible in solutions for analysis on account of the danger from chlorine, hypochlorous acid or hypochlorites. If a depolarizer for chlorine, like toluene, xylene or silver, is used the difficulties disappear except perhaps in some determinations of copper.

(8) A great deal more experimental work needs to be done before we understand all the problems connected with electroplating and electrolytic analysis, but the general principles seem to be fairly well established.

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