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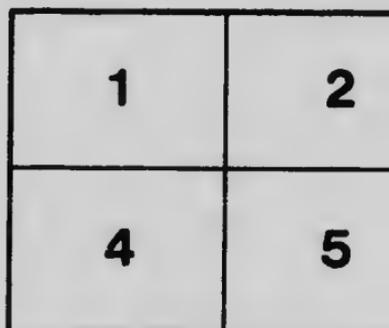
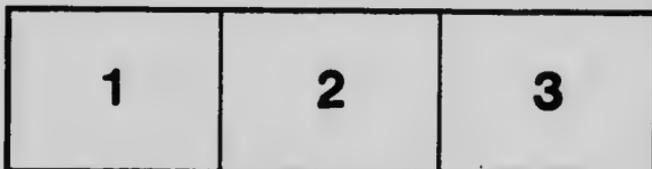
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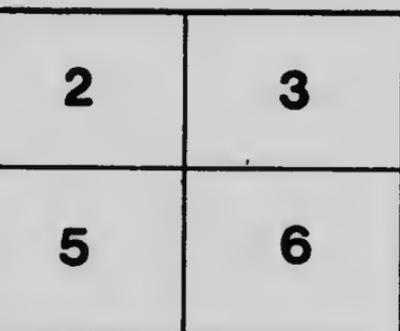
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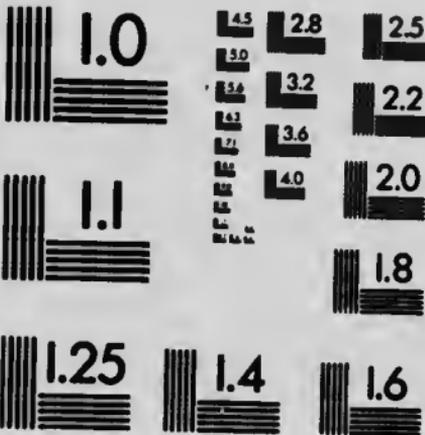
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PAPERS FROM THE CHEMICAL  
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No. 107: ON THE FORMATION OF A BADLY CONDUCTING  
FILM ON COPPER ANODES IN COPPER CYANIDE SOLU-  
TIONS, BY W. LASH MILLER

(REPRINTED FROM THE TRANSACTIONS OF THE AMERICAN ELECTRO-CHEMICAL SOCIETY, 1914)

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*A paper presented at the Twenty-sixth General Meeting of the American Electrochemical Society, at Niagara Falls, October 3, 1914, President F. A. Lindbury in the Chair.*

## ON THE FORMATION OF A BADLY CONDUCTING FILM ON COPPER ANODES IN COPPER CYANIDE SOLUTIONS.

By W. LASH MILLER.

While preparing some experiments for the laboratory of the Toronto Branch of the American Electroplaters' Society, a current about one ampere was sent through a copper cyanide bath (see below) using strips of copper 9 cm. x 3 cm. as electrodes, the 110 volt D. C. lighting circuit as source of current, and a 32 c. p. carbon filament lamp as resistance in the circuit. The lamp, bright at first, within a minute's time burned dim, the evolution of hydrogen at the cathode fell off, and a voltmeter set over the cell showed a potential difference of 45 volts. On examination, the anode was found to be coated with a smooth yellow-green adherent deposit; and a few simple trials soon showed that the resistance of this film was the cause of the drop in current.

The formation of such a deposit evidently sets an upper limit to the current density at the anode that can be used efficiently with any given bath; a number of solutions recommended in the literature, which had been made up for another purpose, were tested from this point of view.

It was soon found, as expected, that the current density at which a noticeable film is formed depends on the shape and position of the anode and on the amount of circulation in the electrolyte; the simple apparatus shown in Fig. 1 was then constructed, and the various electrolytes were compared under the conditions obtaining in it.

In the figure, *A* is the anode, a cylinder of copper rod 2 cm. in diameter, *C* is the cathode, a hollow cylinder of sheet copper 2 mm. thick, 4 cm. internal diameter, slit down one side so that the height of the liquid could be read on a paper scale *S* pasted on the outside of the glass container *G*. Anode and cathode were



held in position by means of two corks, of which the lower, *L*, was provided with a socket to catch the end of the anode and with notches and its edge to let the solution flow out evenly when the tap was opened. The zero mark of the scale was level with the upper side of the lower cork, its graduations ran from 1 to 10, and gave the area of submerged anode in tenths of a square decimeter; division 10 was 2 or 3 centimeters below the upper cork, *U*.



FIG. 1.

To ensure that the liquid would run out of the cell at the same rate in different experiments, a glass nozzle was attached by rubber below the tap, and the latter was always either closed or wide open; with the nozzle used it took the solutions 60 seconds to fall from division 10 to division 1 on the scale, the volume comprised between these two marks being 197 cc.

Before each measurement, anode and cathode were cleaned by nitric acid, washed under the tap, and placed in the container; 250 cc. of an electrolyte was poured in through the funnel, the tap was opened, and as the surface passed division 10, the current (about one ampere) was switched on and its amount recorded. As the level fell, a voltmeter<sup>1</sup> wired across the cell was read; at first the voltage was low, then suddenly began to rise, often with a well marked "jump," whereupon the circuit was broken, the tap closed, and the level recorded; hence the current density when the sudden rise in voltage began was calculated. If the tap were left open, and the current on, the voltage rose rapidly until the needle reached the end of the scale.

Each measurement was made in duplicate, and when it appeared that the initial current was too high, the work was repeated using half an ampere; with baths 5, 11 and 13 a still smaller current would have been better.

The amount of "jump" and the rapidity of the rise in voltage varied from case to case; in every case examination of the anode showed that a precipitate had been formed there, but the color of the deposit varied from yellow to green and brown, and its appearance from smooth and coherent to streaky, depending on the composition of the electrolyte.

<sup>1</sup> Reading from 0 to 3 volts graduated to one fiftieth volt.

The following table gives the compositions of the solutions employed; the last three columns give the number of grams of "free cyanide" per litre determined as recommended by Langbein, with volumetric silver nitrate and sodium chloride as indicated—the current density in amperes per square decimeter at the anode when the voltage jumps occurred, and the result of the "copper titration" described below.

Bath No.	Copper salt used	Composition of Bath					Free Cyanid.	Current Density	Copper Titration
		Grams per litre Cu.	Grams per litre KCN	Grams per litre NaHSO <sub>3</sub>	Grams per litre K <sub>2</sub> CO <sub>3</sub>	cc. of 3% H <sub>2</sub> O 0.5% per litre			
1	Sulphate	12.5	12.5	0	0	55	80.0	3.0	33.0
9	Sulphate	4.6	53.5	0	S* 72	0	56.0	1.75	22.6
8	Carbonate	27	100	25	25	0	13.5	1.33	18.0
15	.....	23	.....	.....	.....	.....	5.0	1.3	16.2
3	Acetate	14	53.3	44	S* 7	0	10.5	1.25	13.3
7	Carbonate	20	75	15	15	0	28.0	1.25	13.0
4	Carbonate	14	53.5	0	0	0	15.5	1.1	7.7
14	.....	9	.....	.....	.....	.....	13.8	1.0	6.8
6	Sulphate	9.5	38	0	0	26	16.0	1.0	4.3
2	Sulphate	6.5	21.4	18	S* 48	0	6.3	1.0	4.0
13	.....	45	.....	.....	.....	.....	6.0	0.5	2.2
11	Acetate	5.1	20	0	0	10	6.0	0.7	2.1
5	Acetate	6.3	19.6	24	40	8	13.7	0.55	0.9

## NOTES:

- S\* denotes crystallized sodium carbonate.  
 In bath 2 the bluestone was precipitated by the carbonate and the resulting sodium sulphate washed out.  
 Bath 9 contained 36 grams crystallized sodium sulphate per litre.  
 Bath 11 contained 12 grams crystallized sodium thiosulphate per litre.  
 Baths 13, 14, 15 were supplied by members of the Electroplaters' Society; the others were made up from receipts found as follows:  
 1. Watt and Phillip, *Electroplating and Refining of Metals*, D. Van Nostrand Co., New York (1902), p. 155.  
 2. Langbein, *Electrodeposition of Metals* 5th ed., Philadelphia, 1905, p. 323.  
 3. Langbein, l. c. 322.  
 4. Bennett, *Trans. Am. Electrochem. Soc.*, 23, 237 (1913).  
 5. Langbein, l. c. 303; Bennett, l. c. 241.  
 6. Bennett, l. c. 239.  
 7. Bennett, l. c. 240.  
 8. Bennett, l. c. 240.  
 9. Bennett, l. c. 241.  
 11. Bennett, l. c. 242.

Inspection shows that the numbers under "current density" and those under "free cyanide" do not run parallel; the current density at which a film is formed cannot be predicted from a knowledge of the solubility of silver chloride in the solution. It seemed probable, however, that in every case the formation of a precipi-

tate was due to the same cause. At each square centimeter of the anode surface copper salt is entering the solution at a rate proportional to the current density, and is being carried away into the bulk of the liquid by diffusion and convection; the concentration of copper in the solution at the anode surface will therefore be greater than in the body of the electrolyte, and the difference will increase with increase in the current density. Now, in all the solutions employed, a sufficient increase in the copper concentration causes a precipitate; it therefore seemed probable that solutions in which a small amount of additional copper salt produced a precipitate would give the voltage jump with a low current density, and vice versa.

To test this conclusion, a solution was made up containing 8.00 g. crystallized copper chloride per liter, which was added from a burette to five cubic centimeters of each of the solutions of the table, until a precipitate appeared. In most cases the latter looked blue through the liquid, some, however, were white or yellowish, and one (from No. 11, which contained thiosulphate) was brown; the "end point" of the titration was not very sharp. The number of cubic centimeters of copper solution used is entered under "copper titration" in the table, and comparison of these numbers with those under "current density" shows that the two series run together; by means of a graph it is possible from the burette reading to interpolate very closely the current density at the anode that with any given solution will cause the voltage jump. Not only cyanide, but ammonia or any other substance that holds the copper in solution, can thus be added to the bath to permit the use of a high anodic current density.





