ELECTRODEPOSITION OF COPPER UPON IRON

BY OLIVER W. BROWN AND FRANK C. MATHERS

Most common metals as iron or zinc will precipitate copper when simply immersed in an acid copper-plating solution. This always results in a non-adherent deposit of copper of no value to the plater. Under the same conditions, iron and zinc have no effect upon an alkaline cyanide bath. The acid-plating solutions are always used where the cathode materials as copper, lead, carbon, etc., make it possible, because of their very high efficiencies and the high current densities at which they will work. But with iron or zinc cathodes, alkaline copper baths must be used. All of the alkaline copper-plating solutions recommended by Pfanhauser in "Elektroplattirung," page 332, contain cyanide. Cyanide is objectionable, both on account of its very poisonous properties and its high cost. In the case of cyanide copper-plating solutions, the anode soon becomes covered with a slimy green precipitate, which causes bad local action, interferes with the proper working of the bath, and may reduce the efficiency of anode corrosion. This green precipitate causes very unequal corrosion over the surface of the anodes, resulting in deep pitting. The bath voltage is also greatly increased. The formation of the precipitate over the surface of the anode can be prevented only by the addition of large amounts of cyanide. Pfanhauser states that the current efficiency of his cyanide copper-plating bath is 80 percent. This probably refers to the cathode, as no mention is made of anode corrosion. When the bath becomes old the efficiency drops considerably below 80 percent.

In our experiments the plating solution was placed in a glass battery jar, 12 cm. long, 15 cm. high, and 6 cm. wide. The volume of the plating solution was generally about 700 cc. A copper voltameter was always placed in series with the plating bath. The electrodes of the bath were connected to a switchboard, normal calomel electrode and standard cells, arranged for measuring the discharge potentials of the cathode, of the anode,

and also the total polarization electromotive force of the bath.   In
the calculations, the value of the calomel electrode was taken
as —0.56 volt.   Unless otherwise stated, the electrodes were
100 sq. cm. area on one side.   Iron cathodes were tried in each
bath in order to observe the quality of the copper deposited upon
iron, but copper cathodes were used in making measure-
ments for the tables and for quantitative experiments.   The
electrodes were placed 5 cm. apart, unless otherwise stated, and
the solution was not stirred during electrolysis.

The beautiful and firm deposit obtained in the ammonia
method for the quantitative determination of copper, suggested
that a similar solution might make a good plating bath for the
deposition of copper upon iron.   A bath of the following
composition was tried :

> 100 grams copper sulphate,
> 120 cc ammonium hydrate,
> 1000 cc water.

This bath attacked iron cathodes, and the anode was always
covered with a basic copper slime during electrolysis, which
made quantitative work impossible.   Experiments were also
made with an ammonia-bath containing

> 60 grams copper sulphate,
> 66 cc ammonium hydrate,
> 1000 cc water

This bath gave equally poor results even with as low a current
density as 0.2 ampere per square decimeter.   However, both of these
solutions gave excellent deposits of copper upon copper cathodes.
The addition of more ammonia and ammonium salts did not
improve the working of the baths.

The "Weil" bath, described in Langbeins's "Electrode-
position of Metals," page 229, was next tried.   This bath con-
tains

> 159 grams sodium potassium tartrate,
> 31.5   "   copper sulphate,
> 50.4   "   caustic soda,
> 1000 cc water.

This gives good anode corrosion and fine cathode deposits as long as the current density is not above 0.25 ampere per square decimeter. The deposit upon an iron cathode was as firm, smooth and bright as upon copper. The experimental data with this bath are as follows:

Amp.	Bath tension Volt	Discharge potential		Total polarization E. M. F. of cell Volt	Current efficiency	
		at Cathode Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.25	0.6	0.36	—0.104	0.48	95.2	101.7
0.4	0.8	0.207	—0.192	0.75	—	101.7

In the second experiment the cathode deposit was so spongy that it could not be accurately weighed. To get a bath that would work at a higher current density and also give a better cathode efficiency, the following was next tried:

> 159 grams sodium potassium tartrate,
> 61 " copper sulphate,
> 50 " sodium hydroxide,
> 50 " sodium chloride,
> 1000 cc. water.

With a cathode area of 50 sq. cm. the following results were obtained:

Amp.	Bath tension Volt	Discharge potential		Total polarization E. M. F. of cell Volt	Current efficiency	
		at Cathde Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.306	0.73	0.306	—0.177	0.427	100.88	100.7
0.31	0.75	0.31	—0.161	0.456	101.1	102.2
0.36	0.7	0.36	—0.132	0.39	100.28	100.76
0.32	0.69	0.32	—0.173	0.27	99.48	—
0.32	0.85	0.32	—0.132	0.545	100.6	100.7

In the above experiments the deposited copper was very bright, dense and coherent, and was just as good when deposited upon iron as upon copper. As the cathode used had an area of 50 sq. cm.,

the current density per square decimeter is equal to twice the current strength. The probable cause of the current efficiencies going above 100 percent is the presence of some cuprous salts in the bath. As the bath resembles Fehling's solution, it is easy to see how it might be reduced perhaps by the current itself in any experiment in which the efficiency was below 100 percent or by the introduction of some organic impurity.

When the above bath was diluted with an equal volume of water, the following results were obtained:

Amp.	Bath tension Volts	Discharge potential		Total po-larization E. M. F. of cell Volt	Current efficiency	
		at Cathode Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.225	0.8	0.204	–0.174	0.366	100.91	100.95
0.35	1.71	0.635	0.75	1.44	100.81	15.5
0.34	1.6	0.516	0.693	1.19	101.68	34.1

In the third experiment, 50 grams of salt were added to each 1000 cc. of solution. In the first of these experiments, the precipitate was bright and firm, but in the last two the cathode deposit was black and spongy.

Under certain conditions the anode assumes the passive state and then it does not dissolve but merely becomes covered with a thin coating, probably of cuprous oxide. This is clearly shown in the following experiments, which also illustrate the ease and accuracy by which one can tell what is happening in the bath from the discharge potential readings.

	Amp.	Volts	Cat. disc. Volt	An. disc. Volt	T. polar. Volts	Effic. cath. Percent	Effic. anode Percent
At start	0.55		0.312	0.162	0.481		– – –
At end	0.54	1.6	0.148	0.786	0.716	100.52	39.50
At start	0.42	1.5	0.22	0.81	1.017		
At end	0.42	–	0.163	0.796	0.978	101.02	0.12

After cleaning the anode in nitric acid and washing in water, the discharge potential reading was —0.132 volt. At the be-

ginning of the first experiment the anode was dissolving quan-
titatively as shown by the discharge reading, but the high dis-
charge potential at the end of the experiment indicates that the
corrosion had ceased. The very low anode efficiency of 39.5 per-
cent proves this. The same anode, without any cleaning, was used
in the second experiment in the above table, at a current density
at which it should have dissolved, but the anode discharge
potential, both at the start and at the end, indicates that it was
not dissolving and the anode current efficiency of only 0.12 per-
cent proves this fact. After cleaning the anode in nitric acid,
the discharge reading of —0.132 volt shows that the passive
state of the electrode is removed by the acid treatment.

In using the tartrate-plating solutions, it was noticed that
after a certain lapse of time, they failed to give as good results
as when new, that is, the anode efficiency was not as good at the
higher current densities. The cathode deposit was as bright
and firm as ever. It was first thought that the tartrate was
being used up. However, the addition of more of this salt did
not improve the anode corrosion. It was next thought that the
carbon dioxide of the air was gradually changing the caustic
soda of the bath to sodium carbonate, thus injuring the plating
solution. To test this, a vigorous current of carbon dioxide
gas was passed for ten minutes through a bath, which was in
perfect working order. This solution then gave a black, spongy
cathode deposit and the anode was covered with a green, slimy
precipitate and was deeply pitted. It was impossible to accu-
rately weigh the electrodes. No way of precipitating out the
carbon dioxide by the addition of such reagents as milk of lime
or barium hydrate was found as these substances precipitate
calcium or barium tartrate. Later experiments show that the
addition of as much as 15 grams of caustic soda per liter will
completely restore one of these baths. As an example, the fol-
lowing data is from a bath, which was working badly, to which
was added 15 grams of caustic soda per liter. The cathode sur-
face was 50 sq. cm. With a current of 0.2 ampere and a vol-
tage of 0.9, the cathode discharge potential was 0.266 volt, the
anode discharge potential was —0.133 and the total polarization

electromotive force was 0.459. The cathode efficiency was 100.12 percent and the anode efficiency was 102.42 percent. The cathode deposit was bright and firm.

In order to get a plating solution which would not change composition on contact with air, several baths were made containing sodium carbonate instead of caustic soda. In all of these the cathode deposit was smooth and adherent, but the anode did not dissolve. Salt, sodium carbonate, potassium chlorate, and tartrates were added, temperatures from 30 to 85° C, and high and low current densities were tried but in no case did the anode appreciably corrode.

A bath of the following composition has given good results, when plating copper upon iron :

> 159 grams sodium potassium tartrate,
> 60   "   copper sulphate,
> 50   "   caustic soda,
> 50   "   sodium chloride,
> 1000 cc water.

After 136 hours electrolysis with 0.2 ampere and a cathode of 50 sq. cm. surface and an anode of 100 sq. cm., the bath was still giving excellent results. Then after this 136 hours' electrolysis, a current of 0.3 ampere per square decimeter gave an anode discharge of —0.074 volt which immediately changed to —0.88 volt, showing that at this place the anode ceased to corrode. The addition of 15 grams of caustic soda per liter brought the anode discharge to —0.133 volt with a current density as high as 0.47 ampere per square decimeter. This very clearly shows that the addition of caustic soda prevents the formation of slime and restores a high efficiency in anode corrosion.

Experiments were next tried to determine the effect of sodium chloride, sodium potassium tartrate, copper sulfate, and sodium hydroxide upon the copper deposit and also upon the efficiency of anode corrosion. In all of these experiments, one cathode and two anodes of copper, 10 by 10 cm. were used. The two anodes were placed 5 cm. apart and the cathode was hung between them. This gave an active surface of 2 sq. dcm. for

both the cathode and the anode. All readings were taken after 20 minutes' electrolysis.

TABLE I

Effect of varying amounts of sodium chloride. The plating solution contained, copper sulphate 60 grams, sodium hydroxide 50 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of sodium chloride.

Grams NaCl per liter	Bath tension Volt	Amperes per square decimeter at anode and cathode	Discharge potential at cathode Volt	Discharge potential at anode Volt	Total polarization E. M. F. of cell	Nature of cathode deposit
0	0.0	0.0	−0.154	−0.154	0.0	
0	0.38	0.1	−0.212	−0.291	0.229	Bright
0	—	0.35	−0.067	−0.216	—	"
0	0.82	0.4	−0.392	−0.094	0.490	"
0	0.90	0.5	−0.322	−0.098	0.490	Bright
0	1.00	0.6	−0.378	−0.098	0.571	Burned
0	1.30	0.9	−0.490	−0.126	0.761	"
0	1.20	1.04	−0.518	−0.112	0.854	"
0	1.92	1.07	−0.548	−0.686	1.501	"
50	0.43	0.1	−0.0	−0.168	0.241	Bright
50	0.8	0.25	+0.28	−0.140	0.456	"
50	0.89	0.3	+0.296	−0.112	0.414	"
50	1.00	0.4	−0.468	−0.132	0.691	Burned
50	1.2	0.75	−0.845	−0.14	0.913	"
50	1.9	1.0	−0.711	−0.798	1.627	"
100	0.55	0.1	−0.098	−0.134	0.347	Dark
100	1.00	0.3	−0.274	−0.102	—	"
100	1.16	0.4	+0.658	−0.148	0.851	"
100	1.28	0.5	+0.577	−0.151	0.831	"
100	2.11	0.6	+0.784	−0.882	1.753	"

Results in the above table show that with no salt in the plating bath, a current density of 0.1 to 0.5 ampere per square decimeter gave a bright, dense and adherent deposit, which was as good upon iron as upon copper. With 50 grams of salt per liter, good cathode deposits were gotten with currents of 0.1 to 0.3 ampere per square decimeter, while with 100 grams of salt per liter, the cathode deposits obtained at all densities were dark. The anode discharge potentials show that the maximum current density per square decimeter, which will give theoretical

efficiency in anode corrosion, is 1.04 amperes with no salt, 0.75 ampere with 50 grams of salt, and 0.5 ampere with 100 grams of salt per liter. Hence the addition of sodium chloride is harmful to the cathode deposit and decreases the efficiency of anode corrosion, in all cases.

TABLE 2

Effect of varying amounts of copper sulfate. The plating solution contained sodium hydroxide 60 grams, sodium potassium tartrate 159 grams, water 1000 cc. and varying amounts of copper sulfate.

Grams of CuSO₄5H₂O per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode	at anode		
40	0.4	0.1	—0.012	—0.147	0.174	Bright
40	0.98	0.3	+0.269	—0.139	0.47	''
40	1.00	0.4	+0.466	—0.139	0.655	Slightly burned
40	1.35	0.5	+0.466	—0.139	0.63	Burned
40	1.12	0.6	+0.494	—0.144	0.619	''
40	2.2	0.7	+0.409	—0.610	1.125	''
60	0.38	0.1	+0.212	—0.291	0.229	Bright
60	0.9	0.5	+0.322	—0.098	0.49	''
60	1.	0.6	+0.378	—0.098	0.571	Burned
60	1.2	1.04	+0.518	—0.112	0.854	''
60	1.92	1.07	+0.548	—0.684	1.501	''
80	0.4	0.1	+0.03	—0.15	0.202	Purple deposit
80	0.65	0.2	+0.181	—0.147	0.36	Dark
80	0.82	0.3	+0.269	—0.145	0.404	Bright
80	0.95	0.4	+0.269	—0.161	0.410	''
80	1.00	0.5	+0.232	—0.150	0.379	''
80	1.9	0.6	+0.246	—0.799	1.298	Burned

The results in the above table show that with 40 grams of copper sulfate per liter in the plating bath, a current density per square decimeter of from 0.1 to 0.3 amp. gives good cathode deposits ; with 60 grams, 0.1 to 0.5 amp. may be used, while with 80 grams a density of from 0.3 to 0.5 gives good deposits. When using 80 grams of copper sulfate per liter, a current density below 0.3 ampere per square decimeter gave a deposit which had a purple, velvety appearance. The maximum current density

at the anode which would give theoretical anode corrosion was 0.6 ampere for 40 grams, 1.04 for 60 grams, and 0.5 for 80 grams of copper sulfate per liter. The best results at both the anode and the cathode were gotten when 60 grams of copper sulfate per liter were used.

TABLE 3

Effect of varying amounts of sodium potassium tartrate. The plating solution contained copper sulphate 60 grams, sodium hydroxide 50 grams, water 1000 cc, and varying amounts of sodium potassium tartrate.

Grams of Rochelle salt per 1000 cc.	Bath tension volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
100	0.52	0.1	+0.126	—0.194	0.353	Slightly dark
100	0.65	0.2	0.238	—0.182	0.498	" "
100	0.90	0.3	+0.294	—0.194	0.574	Bright
100	0.80	0.4	0.238	0.157	0.577	"
100	1.80	0.5	0.294	0.826	1.349	"
100	2.15	0.6	0.280	0.854	1.326	Slightly dark
159	0.38	0.1	0.212	0.291	0.229	Bright
159	0.9	0.5	0.322	0.098	0.490	"
159	1.0	0.6	0.378	0.098	0.571	Burned
159	1.2	1.04	0.518	0.112	0.854	"
159	1.92	1.07	0.548	0.684	1.501	"
209	0.68	0.1	0.207	—0.125	0.466	Bright
209	0.80	0.2	0.297	0.056	0.522	"
209	0.90	0.3	0.283	—0.056	0.449	"
209	0.80	0.35				Burned
209	1.29	0.4	0.325	0.153	0.632	"
209	1.45	0.7	0.301	—0.153	0.660	"
209	2.10	0.8	0.446	0.743	1.169	"

These results show that the limits for the current densities which will give good cathode deposits are 0.3 and 0.5 ampere with 100 grams, 0.1 and 0.5 with 159 grams, and 0.1 and 0.3 with 209 grams of sodium potassium tartrate per liter. The maximum density, which gives theoretical anode corrosion is 0.4 ampere with 100 grams, 1.04 amperes with 159 grams, and 0.7 with 209 grams of sodium potassium tartrate per liter.

TABLE 4

Effect of varying amounts of sodium hydroxide. The plating solution contained copper sulphate 60 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of hydroxide.

Grams caustic soda per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential at cathode Volt	at anode Volt	Total polarization E. M. F. of cell	Nature of cathode deposit
25	0.7	0.1	+0.258	—0.181	0.525	Bright
25	1.6	0.2	—0.213	—0.883	1.112	"
25	1.7	0.3	—	—	—	"
25	2.0	0.4	—0.213	—0.715	0.936	Dark

Cleaning electrodes in acid gave no better anode corrosion.

35	0.4	0.1	—0.026	—0.158	0.177	Black
35	0.7	0.2	—0.184	—0.181	0.129	Dark
35	0.92	0.3	—0.243	—0.184	0.494	"
35	1.60	0.35	—	—	—	Slightly dark
35	1.80	0.4	+0.297	—0.799	1.256	Bright
35	2.12	0.5	+0.494	—0.855	1.322	Dark
40[1]	0.28	0.05	—0.240	—0.407	0.177	Purple
40	0.5	0.175	—0.130	—0.366	0.341	Bright
40	0.9	0.450	—0.084	—0.028	0.473	"
40	0.95	0.50	+0.084	—0.014	0.526	Dark
40	1.00	0.55	—0.084	—0.519	1.23	"
40	2.00	0.6	+0.052	—0.615	1.372	"
45	0.4	0.1	—0.126	—0.35	0.294	"
45	0.7	0.2	—0.028	—0.168	0.35	Bright
45	0.9	0.5	+0.084	—0.098	0.462	"
45	1.3	0.6	+0.336	—0.084	0.644	Dark
45	1.1	0.8	—0.112	—0.028	0.665	"
45	1.8	0.9	—0.089	—0.616	1.23	"
50	0.38	0.1	—0.212	—0.291	0.229	Bright
50	0.9	0.5	—0.322	—0.098	0.49	"
50	1.0	0.6	—0.378	—0.098	0.571	Burned
50	1.2	1.04	+0.518	—0.112	0.854	"
50	1.92	1.07	—0.548	—0.684	1.501	"
55	0.3	0.1	—0.238	—0.387	0.174	Dark
55	0.6	0.2	—0.112	—0.244	0.316	Bright
55	0.9	0.5	—0.084	—0.126	0.453	Slightly spongy
55	1.1	0.6	—0.224	—0.112	0.588	Dark
55	1.4	1.0	—0.154	—0.196	0.728	"
55	2.0	1.1	—0.154	—0.896	1.36	"

[1] Mr. Henry B. Wilson, Jr. did the experimental work upon the solutions containing 40, 45, and 55 grams of sodium hydroxide per liter.

TABLE 4—(*Continued*)

Effect of varying amounts of sodium hydroxide. The plating solution contained copper sulphate 60 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of hydroxide.

Grams caustic soda per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
60	0.4	0.1	—0.093	0.196	0.207	Dark
60	0.7	0.2	—0.098	0.129	0.378	Bright
60	0.82	0.4	0.252	—0.126	0.52	"
60	1.00	0.5	—0.235	—0.126	0.574	Slightly spongy
60	1.1	0.6	—0.238	0.080	0.761	Dark
60	1.45	0.9	+0.426	0.179	0.621	"
60	2.00	1.0	—0.462	0.658	—	"
70	0.35	0.1	0.037	—0.237	0.271	"
70	0.80	0.2	0.185	—0.125	0.428	Slightly spongy
70	0.8	0.3	0.244	—0.195	0.509	Slightly spongy
70	1.2	0.4	0.269	—0.096	0.705	Dark
70	1.2	0.9	+0.494	—0.195	0.826	"
70	2.16	1.0	—0.494	—0.771	1.408	"

Grams NaOH per 1000 cc.	Bath tension Volt	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E.M.F. of cell	Nature of cathode deposit	Current efficiency at	
			at cathode Volt	at anode Volt			Cathode Percent	Anode Percent
40	0.45	0.17	0.162	0.308	0.322	Spongy		103.7
45	1.00	0.5	0.56	—0.112	0.462	Dark		101.57
45	0.9	0.4	0.0	0.098	0.434	Bright	100.45	---
45	0.9	0.4	0.0	0.126	0.462	"		101.75

At beginning, ...
At end, ...

The results of this table are summed up below.

Grams caustic soda per liter	25	35	40	45	50	55	60	70
Limits of current density per square decimeter, giving good deposits . . .	0.1 to 0.3	0.4	0.17 to 0.45	0.1 to 0.5	0.1 to 0.5	0.2 to 0.4	0.2 to 0.4	Dark at all densities
Maximum current density per square decimeter, giving theoretical anode corrosion	0.1	0.3	0.5	0.8	1.04	1.0	0.9	0.9

These results show that a bath with 50 grams of sodium hydroxide per liter admits of the largest range of current densities, which will give theoretical current efficiencies at both the anode and the cathode and also a bright, adherent deposit of copper.

The above tables show that the best bath is as follows:

> 60 grams copper sulfate,
> 50 '' sodium hydroxide,
> 159 '' sodium potassium tartrate,
> 1000 cc water.

The best working conditions for the above bath are a current density at the cathode of 0.1 to 0.5 ampere per square decimeter and a maximum density per square decimeter at the anode of not over 1.04 amperes. If at any time a green precipitate should begin to form on the anode, a little caustic soda—three or four grams per liter—should be added. The substitution of potassium hydroxide for sodium hydroxide and the warming of the bath were detrimental to its working. Rolled, electrolytic, and cast copper anodes worked equally well. Under the conditions of the above experiments, the anode ceases to give theoretical corrosion whenever the electrode tension reached a value much above 1.3 volts. In all of our quantitative experiments, the current efficiency for anode corrosion was theoretical if the anode discharge potential had a value of —0.3 or less, but whenever the value changed to —0.6 volt or greater, the anode corrosion became very poor.

The tartrate baths are superior to the cyanide baths, in that they are non-poisonous, do not give off an offensive gas during electrolysis, will work at a higher anode density, give as good cathode deposits, require a lower voltage, and yield a current efficiency of 100 percent at both electrodes.

The bath requires the addition of small amounts of caustic soda from time to time. However, it is not inferior to the cyanide bath in this respect as the latter requires the addition of potassium cyanide.

Electrochemical Laboratory of Indiana University,
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