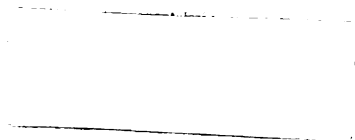
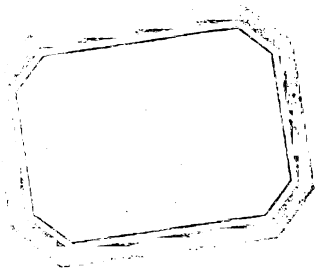




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THE ELECTRODEPOSITION
OF BRIGHT COPPER

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Henry Vincent Pfeuffer Jr.
1947



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OF BRIGHT COPPER

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Henry Vincent Pfeuffer Jr.

has been accepted towards fulfillment
of the requirements for

M. S. degree in Chemistry
(Physical)

J. E. Ewing
Major professor

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THE ELECTRODEPOSITION OF BRIGHT COPPER

by

HENRY VINCENT PFEUFFER Jr.

A THESIS

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Two major types of solutions are available for the electrodeposition of copper. These are: 1. Acid solutions of copper salts; 2. Alkaline solutions of copper salts. The electrodeposition of bright copper is possible in both types of the above mentioned solutions, the majority being of the alkaline type solution.

The acid type bright copper solutions may be classified as follows:

- 1. Solutions containing cupric sulphate, sulphuric acid, and brightening agents.
- 2. Solutions containing cuprous copper salts.
- 3. Solutions of copper salt of sulfonic type acids.
- 4. Solutions of copper salt of dibasic organic acids.

Alkaline bright copper solutions fall into the following classes:

- 1. Cuprocyanide solutions containing brightening agents.
- 2. Solutions of copper amines.
- 3. Copper pyrophosphate solutions.
- 4. Copper sulfamate solutions.

This investigation is limited to the first three types of alkaline bright copper solutions. One typical solution of the cyanide type and pyrophosphate type was investigated for the effects on brightness of temperature, current density, pH, and metallic impurities. The same effects were studied for two types of copper amine solutions, namely, the ethylene diamine and diethylene triamine solutions. A further study was made of the ethylene diamine solution in an effort to improve the throwing power, smoothness of deposit, and brightness of

deposit.

The electrodeposition of bright copper has been extensively studied since 1939. Prior to this time various modifications and additions were made to the existing copper solutions without any notable degree of success in obtaining lustrous, smooth deposits. Kern (1) and Bennett (2) found that the addition of certain colloidal substances and reducing agents to the acid sulphate solution improved the physical appearance of the deposit. Gelatin, tannic acid, glue, and tin were the colloids found beneficial, while pyrogallol, benzoic acid, hydroxylamine, and sugar were the reducing agents used. McCullough and Gilchrist (3), by the addition of Rochelle salts to the cyanide copper bath, improved the brightness, smoothness, and cathode current efficiency. Work of this nature was carried on intermittently until 1936 when Brockman and his co-workers (4,5,6) published the results of a series of investigations on various copper-amine complexes. This research stimulated the subject of bright copper electrodeposition to a considerable extent. Various solutions containing mono, di, and tri ethanolamine, ethylene diamine, and diethylene triamine were studied. The triethanolamine solution, when used in conjunction with sodium oxalate, was found to be applicable for striking steel preparatory to plating in a conventional solution. The ethylene diamine and diethylene solutions, however, gave lustrous deposits even for high current densities. Greenspan (7) improved Brockman's diethylene triamine bath, modifying it by the addition of ammonium sulphate, ammonium hydroxide, and a wetting agent. Similar

modifications have been made to the ethylene diamine solution by Wilson (8) and Hartford (9). Wilson added boric acid and lactic acid to the original Brockman solution while Hartford approximately tripled the original constituents. Coincident with the work on the amine solutions was the development of two successful solutions for bright copper electrodeposition. One was a product of the duPont company (10) and was essentially a cyanide solution containing copper cyanide, potassium cyanide, potassium hydroxide, a brightener (sodium thiocyanate), and an antipitting agent. The solution, when used hot, gave bright deposits up to high current densities. A solution was described by Starek (11) and Coyle (12) and consisted of copper pyrophosphate, potassium pyrophosphate, ammonia, and citric acid. Starek has disclosed the use of dibasic organic acids or their ammonium or fixed alkali salts as brighteners in this solution. Additional brighteners and addition agents listed are the disulfonic acids of phenol or naphthalene and the chlorides of arsenic, bismuth, iron, chromium, tin, zirconium, lead, cadmium, and the alkali metals. The use of a double salt of sodium and copper pyrophosphate as the major constituent of a copper solution has been described by Gamov and Fomenko (13). Other solutions of recent development which are claimed to give bright deposits are as follows: 1. acid copper bath containing thiourea and molasses (14); 2. oxalate-copper complex bath (15); 3. cuprous chloride-sodium thiosulfate solution (16); 4. copper-alkane sulfonic acid solution (17). The latter solution was discussed in an article recently and appears to be applicable for the high

speed deposition of bright copper. A bright cyanide solution was recently developed by Mac Dermid Incorporated (18) containing a salt similar to Rochelle salts and a brightener.

Several theories for the mechanism of bright electrodeposition have been proposed. Taft (19), Bancroft (20), and Kern (21) are of the opinion that addition agent or brightening action falls into one of two classes, namely, adsorption of a colloidal particle with the metal, or reduction of the metal by the particle with no co-deposition. Mathers (22) proposes a complex^x ion formation resulting in a refined grain size. Hunt (23) and Hendrick (24) state that the interference film formed at the cathode interface determines the grain size and thereby the brightness of the deposit. The ratio of this film to the copper ion is said to be the determining factor on the ultimate grain size.

EXPERIMENTAL

Because of the number of processes investigated, each solution will be discussed separately as regards composition, purification, apparatus, and discussion of results.

Ethylene Diamine Solution - The composition of the solution used in each case was as follows:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	- 50 g./l (6.8 oz/gal.)
Ethylene Diamine (60%)	- 42 cc./l (5.4 ")
Ammonium Sulphate	- 10 g./l (1.4 ")
Ammonium Hydroxide	- 23 cc./l (3.1 ")
pH (electrometric)	- 10.0

This is essentially the Brockman (6) solution with ammonium sulphate added as suggested by Greenspan (7). The ammonium hydroxide, copper sulphate, and ammonium sulphate used were of C. P. grade. The ethylene diamine was the Eastman Practical grade.

The chemicals were dissolved in 1 liter of water in the order given. The solution was then purified by filtering hot (50°C) through a slurry of filter aid and activated carbon. This treatment removed organic impurities and suspended matter. The metallic impurities were removed by electrolyzing a dummy cathode of large area at a current density of 2-5 amps/sq.ft. for 5 amp.-hours.

The data for Table II was determined in a 1 liter battery jar. The cathode was suspended between 2 rolled copper

anodes at a distance of 2.5 inches from each anode.

All runs in Tables I, III, and IV were made in the Hull cell using 250 cc. of solution. The cathodes used through-out were steel panels, 4 inches by 2.5 inches. The steel panels were well buffed and electrocleaned c~~m~~ethodically in a hot solution containing 8 ounces per gallon of Northwest 30-45 cleaner. After being electrocleaned, the plates were first rinsed in cold running water followed by an acid dip in 50% hydrochloric acid by volume and finally were rinsed again in cold running water. They were then given a copper strike in a cyanide bath. The criteria used to determine the cleanness of the plate was the water film test. If the plates showed no break in the water film they were immediately placed in the plating solution with the current on. This procedure was used throughout the entire investigation. After each run the solution was filtered through filter aid and the pH checked. All pH determinations were made with the Beckman pH Meter, Model G. To obtain pH values below 8.3, 50% sulphuric acid by volume was added until the value desired was reached. When the preceding run was completed, the solution was discarded and the pH values above 8.3 were obtained by the addition of ethylene diamine (60%). In all cases the free ammonium hydroxide was maintained.

After a preliminary determination of the effect of agitation on the deposit, moderate mechanical agitation corresponding to approximately 20-40 ft./minute was used.

The metallic impurities were added by means of standard solutions of their sulphate salts containing 1 mg/cc. of the

metal. After each run the solution was purified by filtration and electrolysis.

Table I

Ethylene Diamine

THE EFFECT OF TEMPERATURE ON BRIGHT RANGE OF DEPOSIT

Time-ten minutes, Hull Cell, Current-1 ampere

Plate No.	Temp. in C°	Condition of Deposit
1	25°	Bright Range-5 to 25 amps/ft ²
2	30	" " -Same
3	35	" " -Same
4	40	" " -5 to 30
5	45	" " -5 to 45
6	50	" " -5 to 55-very bright
7	55	" " -5 to 55
8	60	" " -5 to 50
9	65	" " -5 to 40-Milky

Table II

Ethylene Diamine

THE EFFECT OF CURRENT DENSITY ON BRIGHTNESS OF DEPOSIT

Temperature-50-60°C, Time-ten minutes

Plate No.	Current Density	Condition of Deposit
10	5 amps/ft ²	Bright-even
11	10	" "
12	15	" "
13	20	" "
14	25	" "
15	30	" "
16	35	" "

Table II (cont'd)

Plate No.	Current Density	Condition of Deposit
17	40 amps/ft ²	Very Bright
18	45	" "
19	50	" "
20	55	" "
21	60	Milky-burned on edges

Table III

Ethylene Diamine

THE EFFECT OF pH ON BRIGHTNESS RANGE OF DEPOSIT

Temperature-50°C, Current-1 ampere, Time-ten minutes

Plate No.	pH	Condition of Deposit
22	7.4	Non adherent-milky
23	7.6	Rough-burned at high C. D.*
24	7.8	Non adherent-burned
25	8.0	Streaked-brittle
26	8.2	" "
27	8.4	" "
28	8.6	" "
29	8.8	Milky-brittle
30	9.0	" "
31	9.2	Bright Range 15-25 amps/ft ²
32	9.4	" " 10-30
33	9.6	" " 10-45
34	9.8	" " 10-55

* C. D. -current density

Table III (cont'd)

Plate No.	pH	Condition of Deposit
35	10.0	Bright Range 10-55
36	10.2	" " 10-55
37	10.4	" " 10-50
38	10.6	Streaked-rough

Table IV

Ethylene Diamine

THE EFFECT OF METALLIC IMPURITIES ON BRIGHT RANGE

Temperature-50°C, Current-1 ampere, Time-ten minutes

1. Nickel

Plate No.	Conc. of Ni(mg./l)	Condition of Deposit
39	1	Bright Range 5-55 amps/ft ² , even
40	2	" " same "
41	4	" " " "
42	8	" " " "
43	16	" " " "
44	32	" " " "
45	64	" " " "
46	128	" " " "
47	256	" " " "
48	500	" " " "
49	1 g./l	" " " "

2. Zinc

Plate No.	Conc. of Zn(mg/l)	Condition of Deposit
50	1	Bright Range 5-55 amps/ft ² , even
51	2	" " same "

Table IV (cont'd)

2. Zinc

Plate No.	Conc. of Zn(mg./l)	Condition of Deposit
52	4	Bright Range 5-55 amps/ft ² , even
53	8	" " Same "
54	16	" " " "
55	32	" " " "
56	64	" " " "
57	128	" " " "
58	256	" " " "
59	506	Rough at high C. D.
60	1 g./l	Treed at high C. D.-rough

3. Iron

Plate No.	Conc. of Fe(mg./l)	Condition of Deposit
61	1	Bright range 5-55 amp/ft ² , even-smooth
62	2	" " Same "
63	4	" " " "
64	8	" " " "
65	16	Bright range 10-50 amp/ft ²
66	32	Pitted-same bright range
67	64	Brittle and pitted-same bright range
68	128	" " "
69	1 g./l	Treed at high C. D.-pitted

Discussion of Results.--The optimum operating conditions evident from the data are as follows:

Temperature - 50 to 55°C

Current Density - 20 to 55 amps/sq. ft.

pH - 9.8 to 10.2

Of the three above variables the one requiring the most careful control is pH. A variation from the 9.8 to 10.2 range causes poor deposits especially if the maximum value of 10.2 is exceeded. pH is, in fact, a measure of the amine to copper ratio, the value of which should be kept at or near 0.8 ($\pm$ 0.03).

Other factors that were found to affect the condition and appearance of the deposit were anode area, ammonia content, and agitation. The anode area required is approximately twice that of the cathode, too little anode area resulting in salt formation on the anode and a resulting decrease in anode corrosion. Addition of ammonia is required frequently as the high temperatures used promote decomposition and subsequent loss of the ammonia.

The brightness of the plate is unaffected by lack of agitation, however, mild agitation is required to prevent the formation of wire-like growths on the cathode. Excess agitation causes streaked deposits.

The deposits from this solution may be classed as lustrous bright and are ductile when free from impurities. Nickel and zinc, in concentrations normally encountered, have little or no effect upon the appearance or properties of the deposit, however, iron, in amounts as low as 16 mg./l, has a harmful effect. The chief effects of iron in concentrations over 32 mg/l are pitting, embrittlement, loss of brightness at low current densities, and treeing at high current densities due to the solid ferric hydroxide particles.

At the optimum operating conditions, the cathode current

efficiency is 107%, indicating some deposition from the cuprous state. The throwing power of the solution is considerably less than that of the standard cyanide solution in spite of the high current efficiency.

Diethylene Triamine Solution.--The composition of the solution used in each case was as follows:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	- 119 g/l (16 oz/gal)
Diethylene Triamine	- 89 " (12 oz/gal)
Ammonium Sulphate	- 18.6 " (2.5 ")
Ammonium Hydroxide	- 30 " (4 ")
Tergitol 08 (wetting agent)	- 2.2 " (.3 ")
pH (electrometric)	- 9.8

This solution (7) is made up in the order shown and purified. The procedure for purifying this solution is identical with that used for the ethylene diamine solution, e.g., filtration through filter aid and activated carbon followed by electrolysis at 2 to 5 amps/sq.ft. for 5 ampere hours.

A 7 liter solution was used for the determination of the effects of temperature and current density upon the deposit (Tables V and VI). This large volume was necessitated by the fact that preliminary investigation showed that abnormal and harmful effects were produced if the current passed exceeded 1 ampere/liter for long periods of time. It was necessary to pass current up to 7 amperes thereby necessitating a large volume. The cathodes used were steel plates with an area of 0.1 square foot. The plates were given a preliminary copper strike in a cyanide bath. Rolled copper anodes were used having an area twice that of the cathode. The anodes were bagged to prevent contamination of the solution by suspended matter. The cathode was suspended in the center of the tank at a distance of 5-3/16 inches from each anode.

The investigation of the effects of pH and impurities was

carried out in a 1 liter beaker using a bent cathode, 1 inch by 4 inches, with a lip 1 square inch in area. The Hull cell was not used because of the inconsistency of results due to contamination from the anode and excessive current used. The cathode was given a preliminary copper strike in a cyanide solution due to iron contamination caused by exposed steel. The procedures for cleaning plates, adding impurities, and varying pH, are similar to those used for the ethylene diamine solution.

Moderate mechanical agitation was used in all cases. Air agitation was attempted but was found to contaminate the solution through the formation of solid oxidation products.

Table V

Diethylene Triamine

THE EFFECT OF TEMPERATURE ON BRIGHTNESS RANGE OF DEPOSIT

Time-ten minutes

Plate No.	Current Density	Temp. in C°	Condition of Deposit
1	40 amp/ft ²	25	Dull-burned on edges
2	40	30	Even-slight milkiness
3	40	35	" " "
4	40	40	Semi-bright
5	40	45	Slightly brighter than #4
6	40	50	Very bright-even
7	50	55	" " "
8	50	60	Dull
9*	50	60	Very bright-even
10	50	65	" " "

* † 30 cc. ammonium hydroxide (conc.)

Table V (cont'd)

Plate No.	Current Density	Temp. in C°	Condition of Deposit
11	50 amp/ft ²	70	Cloudy on edges
12	50	75	" " "
13	50	80	Milky

Table VI

Diethylene Triamine

THE EFFECT OF CURRENT DENSITY ON BRIGHTNESS OF DEPOSIT

Temperature-60°C, Time-ten minutes

Plate No.	Current Density	Condition of Deposit
14	5	Semi-bright
15	10	Very bright
16	15	" "
17	20	" "
18	25	" "
19	30	" "
20	35	" "
21	40	" "
22	45	" "
23	50	" "
24	55	" "
25	60	" "
26	65	" "
27	70	Burned on edges

Table VII

Diethylene Triamine

THE EFFECT OF pH ON BRIGHTNESS RANGE OF DEPOSIT

Temperature-60°C, Bent cathode, Time-ten minutes

Plate No.	pH	Condition of Deposit
28	8.6	Brittle-dull-dark
29	8.8	" " "
30	9.0	Bright Range 5-40 amps per ft ²
31	9.2	" " 5-40
32	9.4	" " 5-40
33	9.6	" " 5-70
34	9.8	" " 5-70
35	10.0	" " 5-60
36	10.2	" " 5-30
37	10.5	Low conductivity-burned at high C. D., milky at others

Table VIII

Diethylene Triamine

THE EFFECT OF METALLIC IMPURITIES ON BRIGHT RANGE OF DEPOSIT

Temperature-60°C, Time-ten min., Current-1 amp., Bent cathode

1. Nickel

Plate No.	Conc. of Ni(mg/l)	Condition of Deposit
38	0	Bright range 5-70 amps/ft ² , even
39	2	" " Same "
40	4	" " " "
41	8	" " " pitted
42	16	" " " "

Table VIII (cont'd)

Plate No.	Conc. of Ni(mg/l)	Condition of Deposit
43	32	Bright range 5-70 amps/ft ² - pitted
44	64	" " Same "
45	128	Bright range 5-50 amps/ft ²
46	256	" " Same
47	1 g/l	" " "

2 Zinc

Plate No.	Conc. of Zn(mg/l)	Condition of Deposit
48	0	Bright range 5-55 amps/ft ²
49	2	" " Same
50	4	" " "
51	8	" " "
52	16	" " "
53	32	" " "
54	64	" " "
55	128	" " "
56	256	" " "
57	1 g./l	Slight Cloudiness

3 Iron

Plate No.	Conc. of Fe(mg/l)	Condition of Deposit
58	0	Bright Range 5-70 amps/ft ² - even
59	2	" " Same
60	4	" " "
61	8	" " "
62	16	Bright Range 10-55-brittle

Table VIII (cont'd)

Plate No.	Conc. of Fe(mg/l)	Condition of Deposit
63	32	Bright Range 15-55 amps/ft ² pitted at all C. D.
64	64	Bright Range 25-50-Fe de- posit low at C. D.
65	128	Poor plate-milky and pitted

Discussion.--The optimum operating conditions as seen from the data are as follows:

Temperature -50 to 60°C

Current Density -20 to 70 amps/sq.ft.

pH -9.5 to 10.0

This solution is extremely sensitive to certain soluble impurities and suspended matter. Iron is the most common impurity and in small amounts produces brittleness and pitting and must be entirely removed before satisfactory deposits may be obtained. Oil, even in small amounts, is taken into solution from the presence of the wetting agent and agitation and causes milky, streaked deposits. The suspended impurities may be introduced through unbagged anodes, exposed steel, and improper filtering technique. Their effect is to cause a general roughness and pitting on the deposit and treeing at high current densities. All of these impurities may be removed by filtration and electrolysis treatment. The effect of the wetting agent, "Tergitol 08" is to increase the tolerance for solid impurities.

As in the ethylene diamine solution the ammonia content is rapidly depleted and must be replenished periodically. A low ammonia content causes a narrowing of the bright range,

while an excess, as determined by odor, has no harmful effect.

The deposits produced in this solution may be classed as lustrous bright, and are the brightest deposits encountered in any of the solutions investigated. The solution has good throwing power and has a cathode current efficiency of 109% at the optimum operating conditions.

As in the case of the ethylene diamine solution, pH is an indication of the amine to copper ratio. When the pH falls below 9.0, dark brittle deposits result. At pH values over 10.0, a narrowing of the bright range is evident.

The following summary gives precautions and operating conditions necessary for satisfactory results from the diethylene triamine solution.

1. Anodes must be bagged at all times.
2. Anodes must be removed from solution when not in use, to prevent dissolving action of solution.
3. Excess ammonia content must be maintained.
4. Current should not exceed 3 amperes/gallon.
5. Solution must be free from organic impurities and metallic impurities, especially iron. Continuous filtration is recommended.
6. Best pH range is 9.5 to 10.0.
7. Best operating temperature is 60°C (140°F).
8. Maximum current density at the above temperature is 70 amps/sq. ft.
9. Mechanical or solution agitation is necessary for operation at high current densities. Air agitation is unsatisfactory.

10. Steel and zinc work should be given a preliminary cyanide strike.
11. An anode area approximately twice that of the cathode area is recommended.

Pyrophosphate Solution-- The composition of the solution used in each case was as follows:

Copper Pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$)	-110 g./l (14.7 oz/g)
Potassium Pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)	-404 " (50.9 oz/g)
Ammonium Hydroxide	- 3 " (0.4 oz/g)
Citric Acid	- 10 " (1.3 oz/g)
pH (electrometric)	- 8.5

This solution is the same pyrophosphate solution developed by Starek(11).

All of the chemicals used were of C. P. grade. Rolled copper anodes were used. The chemicals were mixed in the order shown, heated to 50°C , and filtered through filter aid and activated carbon. The solution was then electrolyzed from 2 to 5 amp-hours at a current density of 5 amps/sq.ft to remove all metallic impurities.

The Hull cell was used in all cases, with the exception of Table X. In this case, a 1 liter beaker containing 750 ml. of solution was used with the cathode suspended between 2 anodes. The anode-cathode distance was 2 inches. Steel plates 4 inches by 2.5 inches were used and were subjected to the same cleaning treatment as in the ethylene diamine procedure. The methods of adding the metallic impurities is also similar to that used for the ethylene diamine bath.

The pH was varied by means of potassium hydroxide and sulfuric acid.

Moderate mechanical agitation was used in all cases.

Table IX

Pyrophosphate

THE EFFECT OF TEMPERATURE ON BRIGHT RANGE OF DEPOSIT

Time-ten minutes, Hull Cell, Current-1 ampere

Plate No.	Temp. in C°	Condition of Deposit
1	21	Black at high C. D. Bright Range-10-35 amps/ft ²
2	25	" " " "
3	30	Same without burning
4	35	" " "
5	40	Bright Range-5-40
6	45	" " "
7	50	Bright Range-5-50
8	55	" " 0-55
9	60	" " 0-60
10	65	" " 0-60
11	70	" " 0-60

Table X

Pyrophosphate

THE EFFECT OF CURRENT DENSITY ON BRIGHTNESS OF DEPOSIT

Temperature-60°C, Time-ten minutes

Plate No.	Current Density	Condition of Deposit
12	10 amps/ft ²	Smooth-bright-even
13	20	" " "
14	30	" " "
15	40	" " "
16	50	" " "
17	55	" " "
18	60	" " "

Table X (cont'd)

Plate No.	Current Density	Condition of Deposit
19	60 amps/ft ²	Smooth-bright-even
20	70	" " "
21	75	Burned at high C. D.
22	80	Same plus rough and dull

Table XI

Pyrophosphate

THE EFFECT OF pH ON BRIGHT RANGE OF DEPOSIT

Temperature-60°C, Hull Cell, Time-ten minutes

Plate No.	pH	Condition of Deposit
23	7.0	Bright Range 5 to 10 amps/ft ²
24	7.5	" " Same
25	7.8	" " "
26	8.0	" " "
27	8.2	" " "
28	8.4	" " "
29	8.5	" " "
30	8.6	" " "
31	8.8	" " "
32	9.0	" " "
33	9.2	" " 5 to 60-rough
34	9.4	Same-duller
35	9.6	" "
36	9.8	" "
37	10.0	Bright Range 5 to 55

Table XI (cont'd)

Plate No.	pH	Condition of Deposit
38	10.5	Bright Range 5 to 55
39	11.0	Semi Bright Range 5 to 55
40	11.5	" " " "
41	12.0	Entire plate milky

Table XII

Pyrophosphate

THE EFFECT OF METALLIC IMPURITIES ON BRIGHT RANGE OF DEPOSIT

1. Nickel--Nickel was added up to concentrations of 1 gram per liter with no deleterious effects upon the smoothness, brightness or ductility of the deposit.
2. Zinc--The effect of zinc up to concentrations of 1 gram per liter is identical with that of nickel.
3. Iron

Temperature-60°C, Hull Cell, Time-ten minutes

Plate No.	Conc. of Fe(mg/l)	Condition of Deposit
42	2	Bright Range 5-70 amps/ft ² - even
43	4	" " Same
44	8	" " "
45	16	" " "
46	32	" " "
47	64	" " "
48	128	" " "
49	256	Cloudy at low C. D.
50	500	" " " "
51	1 g./l	Bright Range 15-70 amps/ft ²

Discussion--The optimum operating conditions for this solution are as follows:

Temperature - 60°C

Current Density - 20 to 65 amps/ft²

pH - 8.5

This solution is very stable and may be operated for considerable periods of time without requiring replacement of chemicals except for those lost through drag-out. The solution as made up is a very heavy and viscous causing considerable drag-out in normal use.

The deposits obtained from this solution are bright, smooth, and ductile. The solution has good throwing power and has a cathode current efficiency of 100% at the optimum operating conditions.

The tolerance of the solution for metallic impurities is very good, as shown by the data. The chief effect of iron is a diminution of brightness at low current densities at concentrations over 256 mg/l.

An unusual pH range, over which good deposits may be obtained, is an advantageous characteristic of this solution. Another advantage is the good adherence of the copper when plated directly on steel.

Cyanide Bright Copper Solution.--The composition of the solution used in each case was as follows:

Potassium Cyanide	-	74 g./l (9 oz/gal.)
Copper Cyanide	-	49 " (6 oz/gal.)
Potassium Hydroxide	-	8.2 " (2 ")
Rocheltex	-	5% by volume
Brightener	-	2% "
pH (electrometric)	-	13.0

This (18) is a cyanide solution modified by the addition of brightening agents (18). The copper cyanide was of technical grade while the potassium cyanide and potassium hydroxide were of C. P. grade. The composition of the "Rocheltex" and the brightener solution were unknown. Both solution were furnished Macdermid Incorporated.

The chemicals were added in the order shown. The solution was then purified by the usual filtration through filter aid and activated carbon followed by an electrolysis using a low current density (2 to 5 amps/sq.ft.).

Steel plates, 4 inches by 2.5 inches were used as cathodes and were prepared by the same procedure as previously mentioned.

Moderate mechanical agitation was used. The solution was filtered and the pH checked after each run.

The data for Tables XIII, XV, XVI, and XVII was determined in a Hull cell. The data for current density effect was accomplished by the same procedure used in the pyrophosphate solution; e.g., a 1 liter beaker, 750 cc. of solution, anode-cathode distance of 2 inches.

Table XIII

Cyanide

THE EFFECT OF TEMPERATURE ON BRIGHT RANGE OF DEPOSIT

Time-ten minutes, Hull Cell, Current-1 ampere

Plate No.	Temp. in C ^o	Condition of Deposit
1	25	Burned
2	30	"
3	35	Burned at high C.D., milky at low
4	40	Bright Range to 10 amps/ft ²
5	45	" " " 14
6	50	" " " 18
7	55	" " " 30
8	60	" " " 40
9	65	" " " 48
10	70	" " " 60

Table XIV

Cyanide

THE EFFECT OF CURRENT DENSITY ON BRIGHTNESS OF DEPOSIT

Temperature-60^o, Time-ten minutes

Plate No.	Current Density	Condition of Deposit
11	10 amps/sq.ft.	Bright-even
12	20	" "
13	30	" "
14	35	" "
15	40	" "
16	45	Rough at high C. D.
17	50	Burned-rough

Table XV

Cyanide

THE EFFECT OF pH ON BRIGHT RANGE OF DEPOSIT
Temperature-60⁰, Hull Cell, Time-ten minutes

Plate No.	pH	Condition of Deposit
18	11.5	Rough-milky
19	12.0	" "
20	12.6	" "
21	12.8	Bright Range 15-25 amps/ft ²
22	13.0	" " 15-40
23	13.2	" " Same
24	13.4	" " "

Table XVI

THE EFFECT OF METALLIC IMPURITIES ON BRIGHT RANGE OF DEPOSIT

1. Nickel--No detrimental effect was noticed up to a concentration of 1 gram/liter of nickel if the free cyanide is allowed to fall below 0.5 ounces/gallon, concentrations of nickel over 16 mg/liter cause rough, streaked deposits due to the formation of suspended nickel hydroxide.

2. Zinc--The results are the same as for nickel.

3. Iron--

Temperature-60⁰C, Hull Cell, Time-ten minutes

Plate No.	Conc. of Iron (Mg/l)	Condition of Deposit
25	1	Bright Range-to 40 amps/ft ² -even
26	2	" " " Same "
27	4	" " " " "
28	8	Rough at high C. D.
29	16	Bright Range 5-40

Table XVI (cont'd)

Plate No.	Conc. of Iron (mg/l)	Condition of Deposit
30	32	Bright Range 5-40 amps/ft ² -rough
31	64	Rough-milky
32	128	Treed-rough-milky
33	256	" " "
34	1 g./l	" " "

Table XVII

Cyanide

THE EFFECT OF FREE CYANIDE ON BRIGHT RANGE OF DEPOSIT

Temperature-60°C, Hull Cell, Time-ten minutes

Plate No.	Free Cyanide (oz/gal.)	Condition of Deposit
35	0.2	Milky-pitted
36	0.3	" "
37	0.4	Bright Range 5-20 amps/ft ²
38	0.5	" " 5-35
39	0.6	" " 5-40
40	0.7	" " Same
41	0.9	" " "
42	1.0	" " "
43	1.2	" " "
44	1.4	" " "
45	1.6	" " "
46	1.8	Semi Bright Range 5-30
47	2.0	" " " 5-15

Discussion--The optimum operating conditions for the solution are as follows:

Temperature - 50 to 70°C
Current Density - 20 to 40 amps/ft²
pH - 13 to 13.5

The free cyanide content must be maintained within the limits, 0.6 to 1.8 ounces/gallon, to insure bright smooth deposits. An excess of anode area (2:1) is desired to prevent burning of the anode.

By the use of the above conditions, bright, smooth deposits may be obtained up to 40 amps/ft². Continued use of the solution at temperature over 50°C causes a depletion of the free cyanide content through the formation of carbonates, resulting in a pitted, milky deposit. This effect may be avoided by the use of lower temperatures and current densities. The "Rocheltex" and brightener solutions are consumed rather slowly but must be replaced periodically in order to prevent decreased brightness of the deposit. The analysis for "Rocheltex" is identical with that used for Rochelle salts.

The solution has very good throwing power and has a cathode current efficiency of 100% at the optimum operating conditions.

Ethylene Diamine Solutions (Improved)--The effect of variation in concentration of the solution's original constituents, e.g., copper sulphate, ethylene diamine, ammonium hydroxide, and ammonium sulphate, was first determined. After arriving at an optimum composition, various compounds, noted for their brightening action or buffering action, were added in an effort to improve the physical characteristics of the deposit and the throwing power of the solution.

All determinations were made in the Hull cell with the exception of the copper sulphate-ethylene diamine procedure, the data for which was determined in a 1 liter beaker. The addition agents were added directly to the cell and were dissolved, in the case of solids, before the determination was made. A constant volume was restored by evaporation. The addition agents were added in small amounts until an effect was noticed on the deposit. Freshly prepared solutions were used for each addition agent. Chemicals of C. P. grade were used for all cases with the exception of the ethylene diamine which was the Eastman Practical grade.

Cathodes of steel plate, 4 inches by 2.5 inches were used. The plates were cleaned in the same manner as previously mentioned and were given a preliminary cyanide strike.

Moderate mechanical agitation was used in all cases.

Copper Sulphate-Ethylene Diamine Ratio--A water solution containing 120 grams/liter of copper sulphate was prepared and diluted to 500 cc. Ethylene diamine was added until a deep blue coloration was formed. Aliquot 10 cc. portions of ethylene diamine were then added until a total of 80 cc./liter had been

added. Test plates were run after each addition. The deposits in all cases were milky and rough. The solution was then diluted with water, added in portions of 100 cc., until 1 liter had been added. The effect of the dilution was noted after each addition. Bright deposits were obtained at concentrations of 50 to 60 grams/liter of copper sulphate. In order to study the effect of ethylene diamine concentration upon the deposit, a solution containing 60 grams/liter of copper sulphate was chosen.

Table XVIII

Ethylene Diamine (Improved)

Temperature-24°C, Hull cell, Time-ten minutes

Plate No.	Ethylene Diamine	Condition of Deposit
1	30 cc./l	Bright Range 10-15-amps/ft ²
2	35	" " Same
3	40	" " " -darker
4	45	Bright Range 15-30
5	50	" " Same
6	55	Dark
7	60	Dark-burned

The optimum composition was 60 grams/liter of copper sulphate and 50 cc./liter of ethylene diamine. This composition was used throughout the remainder of the investigation.

Table XIX

Ethylene Diamine (Improved)

THE EFFECT OF AMMONIUM SULPHATE CONCENTRATION ON DEPOSIT

Temperature-50°C, Hull Cell, Time-ten minutes

Plate No.	Conc. of (NH ₄) ₂ SO ₄	Condition of Deposit
8	5 g/l	Dark-poor-throwing power

Table XIX (cont'd)

Plate No.	Conc. of $(\text{NH}_4)_2\text{SO}_4$	Condition of Deposit
9	10 g/l	Dark-better T. P.*
10	15	Bright Range 10-20 amps/ ft ²
11	20	" " 10-25
12	25	Treed-burned at high C.P.
13	30	" " " " "

The best results were obtained at a concentration of 20 grams/liter of ammonium sulphate. This concentration was used for the investigation of addition agents classed as brighteners.

*T. P.--throwing power

Table XX

Ethylene Diamine (Improved)

THE EFFECT OF AMMONIUM HYDROXIDE CONCENTRATION ON DEPOSIT

Temperature-50°C, Hull Cell, Time-ten minutes

Plate No.	Conc. of NH_4OH	Condition of Deposit
14	5 cc./l	Bright Range 10-40 amps/ft ²
15	10	" " Same
16	15	" " 5-60
17	20	" " Same
18	25	" " 15-30
19	30	Burned-poor T. P.

The optimum concentration of ammonium hydroxide was 15 to 20 cc./liter and this concentration was used throughout the rest of the investigation.

The previous results were combined giving the following solution for the determination of the effect of brightening agents.

CuSO ₄ ·5H ₂ O	- 60 g./l
Ethylene Diamine	- 50 cc./l
Ammonium Sulphate	- 20 g./l
Ammonium Hydroxide	- 20 cc./l
pH	- 10.5

The bright range of this solution was 5-60 amps /sq.ft.

The following compounds gave matte, burned deposits when present in concentrations over 0.5 grams/liter; 1-naph^htylamine-5-sulfonic acid, urea, acetonitrile, sulfanilic acid, tartaric acid, peptone, albumin, naphthol, acetylsalicylic acid, saccharin, and furfurol. Two wetting agents, "Dupenol" and "Tergitol" were added and were found to give milky, streaked deposits at concentrations over 0.01 grams/liter.

Table XXI

Ethylene Diamine (Improved)

THE EFFECT OF CERTAIN ADDITION AGENTS ON BRIGHTNESS OF DEPOSIT

Temperature -50°C, Hull Cell, Time- ten minutes

1. Formaldehyde

Plate No.	Conc. of HCHO	Condition of Deposit
20	0.4 cc/l	Bright Range 5-60 amps/ft ²
21	0.8	" " Same-brighter
22	1.2	Bright Range 5-60-brighter
23	1.6	" " Same
24	2.0	" " "
25	2.4	" " "
26	2.8	" " Rough
27	3.2	Bright Range 5-55

Concentrations of formaldehyde up to 2.4 cc./liter increase

the brightness of the deposit.

2. Sodium Formate

Plate No.	Conc. of NaHCO_2	Condition of Deposit
28	4 g/l	Bright Range 5-60 amps/ft ²
29	8	" " Same
30	16	" " " milky
31	20	" " " T.P. better
32	24	" " " milky
33	28	" " " "
34	32	Burned at high C.D.-dark

Sodium formate, in concentrations of 20 to 28 grams/liter, increased the throwing power of the solution but decreased the brightness of the deposit. Additions of formaldehyde up to 30 cc./liter to the solution containing 24 grams/liter of sodium formate, had no beneficial effect upon the deposit.

3. Ammonium Citrate

Plate No.	Conc. of $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$	Condition of Deposit
35	2 g/l	Bright Range 5-60 amps/ft ²
36	4	" " Same
37	6	" " " brighter
38	8	" " " T.P. better
39	10	" " "
40	12	" " " lustrous
41	14	" " " "
42	16	" " " milky
43	18	" " " matte deposit

Ammonium citrate increased the brightness of deposit and

the throwing power of the solution up to concentrations of 14 grams/liter. Replacement of ammonium sulphate by ammonium citrate gave dull, burned deposits. Citric acid, up to 40 grams/liter, had no beneficial effect when combined with ammonium citrate, at any of the concentrations of ammonium citrate shown in Table XXI.

4. Rochelle Salts (Sodium Potassium Tartrate)

Plate No.	Conc. of Rochelle Salts	Condition of Deposit
44	1 g./l	Bright Range 5-60 amps/ft ²
45	2	" " Same
46	3	" " "
47	4	" " "
48	5	" " "
49	6	" " " brighter
50	7	" " " T.P. better
51	8	" " " brighter
52	9	" " "
53	10	" " "
54	11	Burned on edges
55	12	" " " and at high current density

Rochelle salts, in concentrations of 7 to 10 grams/liter, gave the most satisfactory deposits of all the addition agents used. The throwing power of the solution, although inferior to that of the cyanide solutions, was notably better than that of the standard ethylene diamine solution.

5. Tin

Tin, added as stannic sulphate, formed a colloidal suspens-

ion which caused an increase of the brightness of the deposit at concentrations below 10 mg./l.

GENERAL DISCUSSION

All of the solutions investigated give bright deposits. The throwing power, tolerance for impurities, ease of maintenance, and conditions necessary for satisfactory deposition, however, vary considerably. The throwing power and brightness of the ethylene diamine solution is improved by the addition of ammonium citrate and Rochelle salts. Tin and formaldehyde improved the brightness but have no effect on the throwing power of the solution. Rochelle salts give the most satisfactory deposits in a solution of the following composition:

CuSO ₄ ·5H ₂ O	- 60 g./l
Ethylene Diamine (60%)	- 50 cc./l
Ammonium Sulphate	- 20 g./l
Ammonium Hydroxide	- 20 cc./l
Rochelle Salts	- 8 g./l
pH	- 10.0

This solution will be referred to as ethylene diamine (B).

A comparative discussion of the solutions investigated as to brightness of deposit, bright current density range, throwing power, impurities, and general operating conditions, follows:

Brightness of Deposit--The deposits encountered in this investigation may be divided into two classes, namely, lustrous bright and bright. The lustrous bright deposits are mirror-like and are characteristic of the amine type solutions, the diethylene triamine solution producing the brightest

deposits of the two. The pyrophosphate and cyanide solutions give bright deposits which lack the high luster of the amine deposits.

Bright Current Density Range--At the optimum operating conditions, the following bright current density ranges were obtained for the solutions investigated:

Table XXII

Diethylene Triamine	- 5-to 70 amps/sq.ft.
Pyrophosphate	- 5 to 70
Ethylene Diamine	- 5 to 50
Ethylene Diamine (B)	- 5 to 50
Cyanide	- 5 to 40

Throwing Power--The throwing power of the cyanide and pyrophosphate solutions is very good at all current densities. The diethylene triamine solution has fair throwing power although less than the cyanide and pyrophosphate solutions. The ethylene diamine solution has poor throwing power. The addition of Rochelle salts improves the throwing power of the ethylene diamine solution.

Impurities--The cyanide and pyrophosphate solutions have a very wide tolerance for iron, zinc, and nickel. Harmful effects are produced by the above impurities only when they are present in large amounts sufficient to form suspended hydroxides. These amounts are over 500 mg./liter. The amine solutions are tolerant to zinc and nickel but are extremely sensitive to iron in amounts over 16 mg./liter. Constant purification of the amine solutions is required due to iron contamination of the solution from the chemicals used and from exposed steel surfaces.

An electrolysis treatment, using low current densities, is the only satisfactory method found completely^{to} purify the amine solutions. Organic impurities, either in the form of amine decomposition products or foreign material, e.g., oil, grease, cleaner solution, and buffing compound, produce milky, dull deposits in the amine solutions when present in smaller amounts. No trouble is encountered in the cyanide or pyrophosphate solutions by organic contamination.

General Operating Conditions--Table XXIII illustrates the optimum operating conditions and cathode current efficiencies for the solutions under discussion.

Solution	<u>Table XXIII</u>			
	Temp.	pH	Cathode Efficiency	Max. C.D.
Diethylene Triamine	60°C	9.8	109%	70 amps/ft ²
Ethylene Diamine	50	10.0	107	50
Ethylene Diamine (B)	50	10.0	102	50
Pyrophosphate	60	8.5	100	70
Cyanide	50	13.0	100	40

The amine solutions require bagged anodes in order to prevent suspended material, formed at the anode, from contaminating the solutions. In all solutions investigated an excess of anode area (2:1) is recommended to prevent burning of the anode. High anode current densities in the amine solutions promote loss of brightness and a decrease in the solution conductivity. Air agitation, harmful in the amine and cyanide solutions, may be used in the pyrophosphate solution, due to its chemical stability. Air agitation, used with the cyanide and amine solutions, causes the formation of solid oxidation products. A preliminary

copper strike on steel parts is unnecessary when using the pyrophosphate or cyanide solutions. Deposition in the amine solutions, however, requires preliminary covering of the steel, due to the rapid corrosion of steel in amine type solutions.

The amine solutions give lustrous bright, smooth deposits but require careful control and maintenance. Conversely, the pyrophosphate and cyanide solutions, while giving less lustrous deposits, are easily controlled and maintained.

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