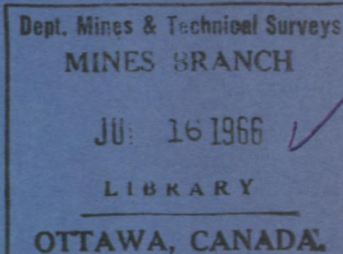


DEPARTMENT OF
MINES AND TECHNICAL SURVEYS
MINES BRANCH



*STABLE COPPER CYANIDE
PLATING BATHS*

W. DINGLEY, J. BEDNAR AND R.R. ROGERS
EXTRACTION METALLURGY DIVISION

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Stable Copper Cyanide Plating Baths*

W. Dingley, J. Bednar and R. R. Rogers**

ABSTRACT

Stable copper cyanide plating baths which can be operated at 25C (77F) have been developed. These conform to both of the following relationships:

- (1) OH^- normality = "free" CN^- normality, and
- (2) $\frac{\text{total NaCN normality}}{\text{Cu normality}}$ varies between 2.6 and 2.9, depending on the bath concentration.

Advantages of these baths include: (1) comparatively simple control of bath compositions. (2) improvement in the nature and adhesion of the copper deposits, and in the plating cell operating conditions. (3) ability to use higher cathode current densities. (4) ability to copper plate high strength steel such as Type 4037 without embrittling the steel. (5) ability to plate comparatively thick copper coatings directly on steel without the use of a "strike" bath.

THE DEMAND FOR COATINGS of electrodeposited copper on steel has been increasing rapidly. It is suspected that this demand would be greater still if high strength steels such as Type 4037 could be electroplated with copper without embrittlement.

Although copper can be electroplated in either acid or alkaline baths, most of the present-day plating is done in the latter type. Alkaline cyanide baths are used extensively for plating copper on steel prior to plating with other metals such as nickel, and for increasing the thickness of copper coatings on steel. Unfortunately the many cyanide baths which have been proposed are unstable, i.e., their compositions change during use.

The present authors have previously found stable cyanide baths for plating zinc and cadmium on steel^{1,2} and it was learned that such baths may be used for plating these metals on high strength steels such as Type 4037 without embrittlement. They now have found stable cyanide baths which can

be used for plating copper on steel. The method of preparing these baths and the information which has been obtained in operating them at 25C (77F) are summarized in the present paper. The results of experiments now being performed at temperatures up to 80C (176F), will be reported later.

Since the present-day practice used in copper plating steel in cyanide baths has been described in some detail by Bair and Graham,³ only a few points of particular importance will be referred to here.

In general, copper plating on steel is done in two stages: (1) plating a thin, comparatively adherent film of copper in a fairly dilute "strike" bath, and (2) building up this film to the desired thickness by further plating in a more concentrated bath which operates at higher cathode current density and higher efficiency. The most important chemicals used in making up these baths are cuprous cyanide (CuCN), sodium or potassium cyanide (NaCN or KCN) and sodium or potassium hydroxide (NaOH or KOH). The baths used in the present research were produced by dissolving cuprous cyanide, sodium cyanide and sodium hydroxide only. Although it may not always be desired, carbonate usually is introduced into the bath as an impurity in the original chemicals or by

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TABLE I
ANALYSIS OF STEEL PINS

Constituent	Per Cent	Constituent	Per Cent
carbon	0.40	molybdenum	0.26
manganese	0.76	phosphorus	<0.02
silicon	0.31	sulfur	0.02

the reaction of atmospheric carbon dioxide with the bath, or as a product of the electrolysis.

A fairly wide variety of additives is used in industrial copper plating baths. However, the use of such materials in the present experimental baths has been avoided even though some of them might have produced an improvement in the results obtained.

Information regarding baths containing potassium compounds has been given in a recent paper by Horner.⁴

According to Bair and Graham,³ most of the copper is believed to exist in the cyanide plating bath in the form of the tri-complex $\text{Cu}(\text{CN})_3^-$, although the di- and tetra- complexes are believed to exist also. The alkali cyanide in excess of the tri-complex salt $\text{Na}_2\text{Cu}(\text{CN})_3$ is termed "free" cyanide.

In the past, the hydroxide has been added to the plating bath primarily to obtain better electrical conductivity, to improve anode corrosion, to adjust the bath pH or to improve the throwing power.

MATERIALS, EQUIPMENT AND PROCEDURES

Electrodes

The cathode materials used in all experiments performed during this research were of two kinds:

- (1) sheets cut from zinc-coated steel Hull cell panels to a size of 6.35 cm (2.5 in.) x 1.27 cm (0.5 in.) x 0.025 cm (0.01 in.). This steel was of the ordinary low carbon variety.
- (2) Type 4037 alloy steel pins 6.35 cm (2.5 in.) long and 0.40 cm (0.15 in.) in diameter having the composition shown in Table I.

The latter had been produced from drawn wire and had been heat treated at 830C (1525F) and quenched in oil, then tempered at 218C (425F) resulting in a Rockwell C hardness of 51-55. When received, they were covered with an extremely porous copper coating and a black smutty material. The surface of the metal was covered with numerous tiny pits which made it quite rough in comparison with the sheet cathodes. This type of pin was chosen for the experiments because in previous work it had proven to be a rather difficult material to plate without embrittlement.

The anodes were of copper which had been cut from bus-bar material. The immersed portion of each one was 10.2 cm (4 in.) x 5.1 cm (2.0 in.) x 1.3 cm (0.5 in.).

Cathode Surface Preparation

Before copper plating, each sheet cathode was treated as follows:

- (1) stripped of zinc by immersion in 18 per cent (by weight) hydrochloric acid produced by diluting concentrated

acid with distilled water. This was performed at room temperature and was continued until vigorous gas evolution ceased.

- (2) rinsed thoroughly in tap water.
- (3) introduced into the plating bath with as little delay as possible.

Each pin was treated by the following procedure, recently developed in this laboratory, which produced a surface which was thoroughly clean, smooth, active and free from embrittlement:

- (1) immersed for 3-5 min in an aqueous solution containing 12 per cent nitric acid and 34 per cent acetic acid by weight.
- (2) rinsed thoroughly in flowing tap water.
- (3) rinsed in water while under the influence of ultrasonic vibration. This was done in an LT-60 transducerized tank energized with a Sonogen ultrasonic generator Model LG-150, 25 kc, 150 watts.*
- (4) rinsed in flowing tap water.
- (5) introduced into the plating bath with as little delay as possible.

Electroplating

The electroplating was performed in two liters of bath in a rectangular glass container 19.0 cm (7.5 in.) long x 12.7 cm (5.0 in.) wide x 12.7 cm (5.0 in.) deep. An anode was placed against each of the narrow (5.0 in.) sides. The cathode, located between the anodes, was supported by a copper-plated steel clip and completely immersed in the solution. The latter was maintained at $25 \pm 2\text{C}$ (77F) and was agitated slowly by a Teflon-coated steel bar which was centrally located at the bottom of the container and rotated by means of a magnetic stirrer. The DC electricity was supplied by a 30 ampere rectifier.

The plating baths were prepared by dissolving sodium cyanide (NaCN), copper cyanide (CuCN) and sodium hydroxide (NaOH) of reagent quality in distilled water. Each one was treated with activated carbon by a procedure described below to remove certain soluble impurities, then filtered through Whatman No. 52 filter paper to remove the carbon and any other solid particles which might be present. The volume of the bath was maintained constant by the addition of distilled water. When required the bath was analyzed in accordance with the procedures given in the *Metal Finishing Guidebook*.⁵

Activated Carbon Treatment

When freshly made up, the plating baths were yellow owing to the presence of certain soluble impurities. An attempt was made to remove this color by adding 5 g/l of activated carbon (charcoal decolorizing powder produced by British Drug Houses), agitating thoroughly and then filtering as already mentioned. Although much of the color was removed in this way, some still remained even after a treatment lasting 24 hr. All color was eliminated, however, when (1) copper anodes and a steel cathode were placed in the bath containing the activated carbon, and (2) the bath was slowly

*Both produced by Branson Ultrasonic Corp.

agitated and electrolyzed for one hour at the maximum current density permissible in that particular bath (See Table V). All baths used in the present research were subjected before use to this preliminary procedure which is referred to as the "E.A.C. treatment."

It may be added that, at the end of the E.A.C. treatment, the anodes are covered with a dark nonmetallic film. If the bath is a stable one, this film can readily be removed by rinsing in water under pressure, revealing a clean, bright surface. If the bath is not a stable one, the dark film will require an acid treatment for its removal.

Coating Thickness Testing

The thicknesses of the electroplated copper coatings were determined by means of the Aminco-Brenner Magne Gage.

Bend Testing of Steel Pins

A slow bend test was used during this investigation to determine: (1) the extent to which the pins had become embrittled during plating, and (2) the adhesion of the copper coating. The test was performed in a Hounsfield notched bar bending jig attached to a Type W tensometer machine equipped with a motor drive.

During the testing, the unnotched pin is supported at two points 3.02 cm (1.19 in.) apart. Pressure applied to a 0.32 cm (0.125 in.) diameter mandrel forces the pin into the gap between these points until it breaks or until a bend of 135° is produced at the end of 11 minutes. The angle at which a pin is fractured, or to which it is bent, is calculated from a chart which operates with the machine. The bending jig originally produced a bend of 90°; however it was modified to give a maximum bend of 135°. Pins that can be bent through this angle without breaking are considered to have passed the test for embrittlement.

EXPERIMENTAL

I. Experiments with Plating Baths Similar to Those Proposed by Previous Investigators

Bath Compositions

A search of the literature^{1, 6} revealed that baths having a wide variety of compositions have been recommended in the past for electroplating copper on steel in cyanide solutions. The analyses presented in Table II are typical. In general, the "strike" baths have had OH⁻ concentrations between 0 and 0.38N and "free" CN⁻ concentrations between 0.12 and 0.31N, and the higher efficiency baths have

TABLE II

ANALYSES OF SODIUM CYANIDE COPPER PLATING BATHS RECOMMENDED BY PREVIOUS INVESTIGATORS (NORMALITY)

Constituent	"Strike Baths"		"Higher Efficiency" Baths	
	Passal	Bair and Graham	Passal	Bair and Graham
CuCN	0.17-0.34	0.17	0.50-1.00	0.55-1.42
NaCN	0.46-0.92*	0.47	1.09-2.34*	1.27-3.14
"Free" CN ⁻	0.15-0.31	0.12	0.11-0.38	0.22-0.39
NaOH	0-0.38	—	0.38-0.95	0.55-0.93
Cu	0.17-0.35*	0.17	0.50-1.0*	0.53-1.40
Na ₂ CO ₃	0-0.42	0.14	0.28-0.71	—

*Calculated by us.

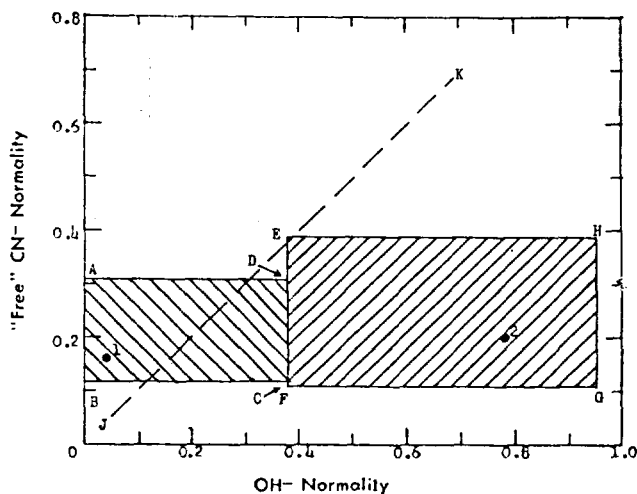


Fig. 1. Range of "free" cyanide and hydroxide normalities of copper cyanide plating baths proposed by previous investigators.

had OH⁻ concentrations between 0.38 and 0.95N and "free" CN⁻ concentrations between 0.11 and 0.39N. These two ranges of compositions are shown as Areas ABCD and EFGH in Fig. 1. During the present research Baths 1 and 2, shown in this figure, were assumed to be fairly typical of the "strike" and higher efficiency baths respectively used by previous investigators. The analyses of these baths are given in Table III.

According to the literature, the ratio

$$\frac{\text{total NaCN normality}}{\text{Cu normality}}$$

has varied between 1.3 and 5.3 in typical "strike" baths used in the past, and between 0.9 and 2.3 in typical higher efficiency baths used in the past.

Stability of Baths 1 and 2

The stabilities of Baths 1 and 2 were determined by electrolyzing samples of them at 25C (77F) using copper anodes and sheet steel cathodes. A cathode current density of 3.2 amp/dm² (30 amp/ft²) was used in the case of Bath 1 and one of 10.8 amp/dm² (100 amp/ft²) in the case of Bath 2, since these approach the maximum values used in present day practice. During each electrolysis, a sample of the bath was removed periodically for analysis for total NaCN, "free" CN⁻, NaOH, Cu and CO₃²⁻ and, at the same time, the copper-coated cathode was replaced by a new one. Typical an-

TABLE III

ANALYSES OF FRESHLY PREPARED BATHS 1 AND 2 (NORMALITY)

Constituent	Bath 1	Bath 2
Cuprous cyanide	0.25	1.34
Sodium cyanide	0.69	2.74
Sodium hydroxide	0.04	0.75
Sodium carbonate	0.01*	0.13
Copper	0.25	1.34
"Free" cyanide	0.15	0.08

*Depends on the purity of chemicals used.

TABLE IV
STABILITY OF PLATING BATHS INVESTIGATED

Bath No.	Time of Plating (hours)	Cathode Current Density (amp/dm ²)	Analysis (normality)					Bath Stability	
			Total NaCN	Cu	Free CN ⁻	NaOH	Na ₂ CO ₃		
1	0	3.2	0.69	0.25	0.23	0.04	Trace	Poor	
	10		0.55	0.39	0.02	0.04	0.18		
2	0	10.8	2.74	1.34	0.12	0.80	0.13	Poor	
	3		n.d.*	1.40	0.05	0.81	0.20		
3	0	2.7	1.35	0.48	0.20	0.20	0.03	Good	
	13		to 3.2	1.35	0.48	0.20	0.20		0.04
	0		to 4.8	4.3	0.48	0.20	0.20		0.04
75	1.35	0.48		0.20	0.20	0.07			
4	0	12.9	1.84	0.65	0.40	0.40	0.07	Good	
	10		1.84	0.65	0.40	0.40	0.07		
5	0	12.9	2.83	1.10	0.60	0.60	0.02	Good	
	14		to 25.8	2.80	1.10	0.60	0.60		0.03

*n.d.—not determined.

analytical results are given in Table IV. It will be noted that, after ten hours of plating at 3.2 amp/dm² (30 amp/ft²), the Cu content of the "strike" bath (Bath 1) had increased considerably and that the "free" CN⁻ content had decreased greatly. In addition the total NaCN content had decreased and the CO₃⁻ content had increased. A similar unstable condition was observed in the higher efficiency bath (Bath 2) after 3 hr of plating at 10.8 amp/dm² (100 amp/ft²). Actually, Bath 2 was found to be unstable even at the lower current density of 3.2 amp/dm² (30 amp/ft²), as shown in Table V.

Embrittlement of High Strength Steel Pins During Plating in Baths 1 and 2

High strength steel pins of Type 4037 were cleaned by a procedure developed in this laboratory, described earlier, which did not produce embrittlement. They then were plated with copper at various cathode current densities in Baths 1 and 2. As shown in Table VI, pins plated in a freshly-made Bath 1 gave no evidence of embrittlement in

the bend test. However, pins plated at the same current density in the same bath after it had been in use for 3 hr were severely embrittled. When the current density was increased the tendency toward embrittlement increased also.

When similar experiments were performed in Bath 2, the tendency toward embrittlement was great in all cases, regardless of the magnitude of the current density or of the time the bath had been in use.

Other Characteristics of Baths 1 and 2

The information presented in Table VII regarding the cell voltage, anode appearance, nature of the electroplated copper, and accumulation of solid salts on the plating cell walls

TABLE VI
RESULTS OF SLOW BEND EMBRITTLEMENT TESTS ON PLATED PINS

Bath No.	Cathode Current Density (amp/dm ²)	Range of Bends Before Breaking (degrees)	Number of Pins	
			Tested	Passed
1	2.1*	>135	6	6
	2.1**	71-135	6	1
	3.2	11-88	6	0
2	2.1	19-90	8	0
	5.4	46-78	4	0
	10.8	18-76	4	0
3	3.2	>135	6	6
	4.3	>135	9	9
4	3.2	>135	6	6
	5.4	>135	6	6
	10.8	>135	6	6
5	5.4	>135	3	3
	12.9	>135	4	4
	25.8	>135	3	3

*freshly prepared bath.
**after bath had been used for 3 hours.

TABLE V
STABILITY OF PLATING BATHS AT DIFFERENT CURRENT DENSITIES

Cathode Current Density (amp/dm ²)	Earlier Baths		Newly-Developed Baths		
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5
3.2	X	X	φ	φ	φ
4.3			φ	φ	φ
5.4			Δ	φ	φ
12.9				φ	φ
14.0				Δ	φ
25.8					φ

X—considerable deterioration (unstable).
φ—no deterioration (stable).
Δ—very slight deterioration.

TABLE VII
CHARACTERISTICS OF UNSTABLE AND STABLE BATHS
AND OF THE RESULTING COPPER DEPOSITS

	Unstable Baths			Stable Baths	
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5
Cell voltage.....	increased	decreased	no change	no change	no change
Anode appearance during plating	dark	very dark	bright, clean	bright, clean	bright, clean
Appearance of deposit after one hour.....	small crystals, quite rough	large crystals, very rough	very tiny crystals, slightly rough	very tiny crystals, slightly rough	very tiny crystals, slightly rough
Thickness of deposit in mils (after one hour except where indicated).....	0.25 at 3.2 amp/dm ² for 15 min. Thicker deposits too rough to measure	too rough to measure at 10.8 amp/dm ²	n.d.*	2.6 (10.8 amp/dm ²)	5.1 (12.9 amp/dm ²); 8.2 (25.8 amp/dm ²)
Adherence of deposit.....	<1 mil thick-- fair >1 mil thick-- poor	very poor at any thickness	very good	very good	very good
Salt accumulation on cell walls and anodes.....	small quantity	considerable	very slight	very slight	very slight
Color of electrolyte.....	turned blue during plating	blue before plating	colorless	colorless	colorless

*n.d.—not determined.

and anodes in the case of these unstable baths indicates that there is considerable room for improvement in their performance.

II. Experiments with Stable Plating Baths

After considerable experimentation it was found that plating baths whose compositions conform to the relationships

- (1) OH⁻ normality = "free" CN⁻ normality
- (2) $\frac{\text{total NaCN normality}}{\text{Cu normality}}$ varying between 2.6 and 2.9 depending on the bath composition (2.8, 2.9, 2.6 for Baths 3, 4 and 5 respectively)

are stable under suitable plating conditions (cathode current density, ratio of anode area: cathode area, etc.).

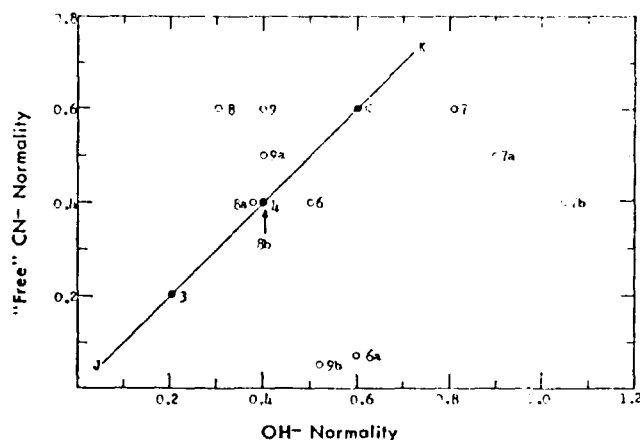


Fig. 2. Effect of plating on the "free" cyanide and hydroxide normalities of typical unstable and stable copper plating baths.

As far as the present authors are aware, these baths are never stable when they are first produced. However, they become stable after they have undergone a certain pretreatment. The nature of this pretreatment is dealt with later under Section III.

The straight line JK, corresponding to Equation (1) above, is shown in Figs. 1 and 2. Baths 3, 4 and 5, lying on this line and having the analyses given in Table VIII, were investigated rather thoroughly to determine the nature of the advantages to be gained from their use. A comparison of Tables III and VIII shows that Bath 3 is more closely related in composition to Bath 1 than to Bath 2, and Baths 4 and 5 are more nearly similar to Bath 2 than to Bath 1.

It is shown in Table IV that the total NaCN, Cu, "free" CN⁻ and OH⁻ contents of Baths 3, 4 and 5 did not change during the plating experiments which were performed. The CO₃²⁻ content increased slightly in some cases. However it is believed, on the basis of past experience, that none of the additional carbonate was produced due to the electrolysis.

TABLE VIII
ANALYSES OF FRESHLY PREPARED BATHS 3, 4
AND 5 (NORMALITY)

Constituent	Bath 3	Bath 4	Bath 5
Cuprous cyanide.....	0.48	0.65	1.10
Sodium cyanide.....	1.35	1.84	2.82
Sodium hydroxide.....	0.20	0.40	0.60
Sodium carbonate*.....	0.03	0.05	0.02
Copper.....	0.48	0.65	1.10
"Free" cyanide.....	0.20**	0.40**	0.60**

*depends on the purity of chemicals used.

**determined after bath had been electrolyzed for 3-4 hours.

Rather it probably was produced by the reaction with carbon dioxide from the air.

Effect of Cathode Current Density on Bath Stability

In Table V evidence is presented that the stability of the plating baths becomes less as higher cathode current densities are used. However, while Baths 1 and 2 were found to be unstable even at the low current density of 3.2 amp/dm² (30 amp/ft²), the newly-developed Baths 3, 4 and 5 were found to be stable at current densities as high as 4.3, 12.9 and 25.8+ amp/dm² (40, 100, 240+ amp/ft²) respectively.

Embrittlement of High Strength Steel Pins During Plating in Baths 3, 4 and 5

As shown in Table VI, there was no evidence of embrittlement in the pins plated in stable Baths 3, 4 and 5 at cathode current densities as high as 4.3, 10.8 and 25.8 amp/dm² respectively. This was a great improvement over the results obtained with Baths 1 and 2. It should be noted that the comparatively small number of results recorded in this table have been borne out by numerous other tests performed during this research.

Other Characteristics of Baths 3, 4 and 5

In Table VII, it is shown that the results obtained with Baths 3, 4 and 5 were much superior to those obtained with Baths 1 and 2.

Importance of Cathode Area: Anode Area Ratio

During the early experiments with the newly-developed plating baths, it was observed that certain baths were stable for a few hours and then became unstable, i.e., the copper content of the bath increased, the "free" CN⁻ content de-

creased, the solution changed from colorless to blue and a nonmetallic film was formed on the anodes. Eventually experiments showed that the ratio of anode area: cathode area must be greater than 4:1 to maintain the new Baths 3, 4 and 5 in a stable state. Satisfactory results were obtained with a ratio of 8:1. In these experiments, the anodes were all copper, not a combination of copper and steel.

III. Production of Stable Plating Baths

When combinations of copper cyanide, sodium cyanide and sodium hydroxide are dissolved in water and the resulting baths are electrolyzed at 25C using copper anodes and steel cathodes, the composition of each bath undergoes a change. Eventually, some of them cease to change, i.e., they become stable. Others continue in the unstable state indefinitely. This is illustrated in Fig. 2 where it is shown that baths in which the OH⁻ normality is higher than the "free" CN⁻ normality do not become stable; also, that only some of the baths (in which the OH⁻ normality originally was lower than the "free" CN⁻ normality) become stable.

Two baths, 6 and 7, lie below the line JK, which represents the baths in which the "free" CN⁻ normality is equal to the OH⁻ normality. On electrolysis, 6 changed to 6a, and 7 to 7a and then 7b. In both cases, the final baths were further from JK than were the original baths.

Two other baths, 8 and 9, are shown above JK. When these were electrolyzed, their "free" CN⁻ normalities changed to 8a and 9a. On further electrolysis, these changed to 8b and 9b. In 8b the "free" CN⁻ and OH⁻ normalities were the same and this bath did not change any further, i.e., it had become stable. On the other hand, 9b had a very much lower "free" CN⁻ normality and a somewhat higher OH⁻ normality than 9a. The "free" CN⁻ normality apparently had been equal to the OH⁻ normality at one time during the electrolysis, but it had not remained that way. It would

TABLE IX
PERFORMANCE OF COPPER PLATING BATHS WHOSE OH⁻ NORMALITIES ARE NOT EQUAL TO THEIR "FREE" CN⁻ NORMALITIES

"Free" CN ⁻ Normality	Bath No.	Time of Plating (hr)	Current Density (amp/dm ²)	Resulting Analysis (normality)					Bath Stability	
				Total NaCN	Cu	"Free" CN ⁻	NaOH	Na ₂ CO ₃		
<1	6	0	10.8	1.9	0.67	0.40	0.51	Trace	Poor	
	6a	6		1.9	0.93	0.07	0.60	Trace		
	7	0	7.4	2.85	1.10	0.60	0.82	0.01	Poor	
	7a	1		n.d.*	1.13	0.55	0.90	0.03		
	7a	0	12.9	n.d.	1.13	0.55	0.90	0.03	Poor	
	7b	3		n.d.	1.20	0.40	1.05	0.06		
	>1	8	0	10.8	1.9	0.67	0.60	0.30	Trace	Poor
		8a	3		1.9	0.67	0.40	0.38	Trace	
8a		0	10.8	1.9	0.67	0.40	0.38	Trace	Good	
8b		4		1.9	0.67	0.40	0.40	Trace		
9		0	12.9	2.85	1.10	0.60	0.40	0.02	Poor	
9a		1		n.d.	n.d.	0.50	0.40	n.d.		
9a		0	25.8	n.d.	n.d.	0.50	0.40	n.d.	Poor	
9b		3		2.76	1.30	0.05	0.52	0.05		

*n.d.—not determined.

appear that the desirable performance of 8a was due to the fact that it followed the requirement that $\frac{\text{total NaCN normality}}{\text{Cu normality}}$ must be some value between 2.6 and 2.9. On the other hand, the different and much less desirable performance of 9a was due to the fact that it did not follow this requirement. More details of these experiments are presented in Table IX. It may be added that none of the higher efficiency baths which have been used in the past meet the requirements of Equation 2. It is possible that some of the "strike" baths used in the past do meet them.

In view of the information given above, it will be realized that a method is required for determining the composition of the initial plating bath to be used in producing a stable plating bath of the desired specifications. The following two graphs are required:

- (1) in which the total NaCN normality is plotted against the CuCN normality in the case of each of the stable Baths 3, 4 and 5. A curve is drawn through the resulting three points (Fig. 3)
- (2) in which the "free" CN^- normality is plotted against the total NaCN normality in the case of each of the three stable baths. A curve is drawn through the resulting three points (Fig. 4)

The recommended method is as follows:

- (1) Decide on the normality of copper cyanide required in the desired stable bath
- (2) Using the curve in Fig. 3, determine the total NaCN normality required by the desired copper cyanide concentration
- (3) Using the curve in Fig. 4, determine the "free" CN^- normality required by the desired total NaCN concentration

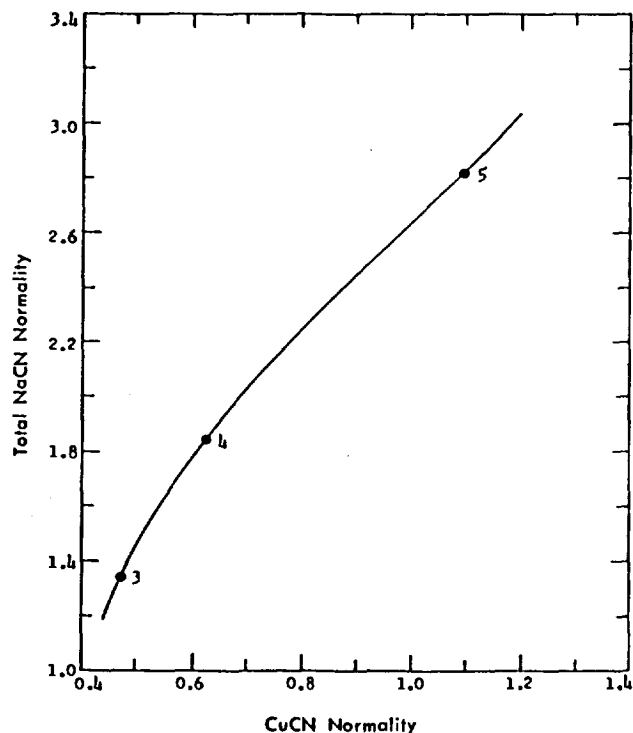


Fig. 3. Relationship between cuprous cyanide and total sodium cyanide normalities in stable copper plating baths.

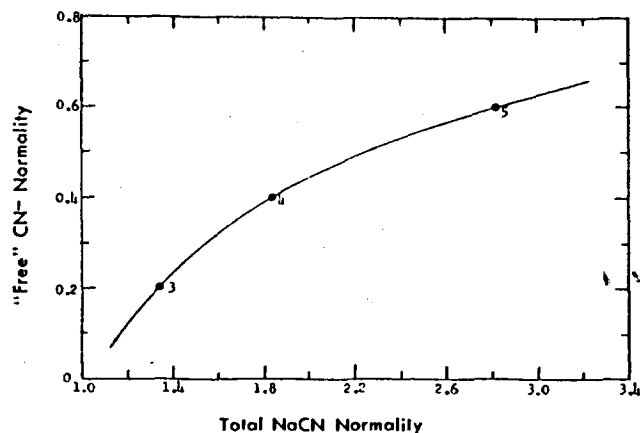


Fig. 4. Relationship between total sodium cyanide and "free" cyanide normalities in stable copper plating baths.

- (4) The NaOH normality required will be equal to the "free" CN^- normality

The validity of this method has been proved in experiments involving plating baths having CuCN normalities of 0.55 and 0.8.

A brief period of instability was observed in the newly developed baths during either an increase or decrease in the cathode current density. Steel pins plated during this period of instability were embrittled and failed in the 135° bend test. This difficulty was overcome by plating on an expendable cathode for a short period during which the current density change was made. Shortly thereafter, pins could be plated without embrittlement. It should be added that embrittlement was not experienced if the current density was changed after the cathode had become covered with copper.

It was found that a stable bath could be rendered unstable by changing the cathode area: anode area ratio to an improper value, or by using too high a cathode current density. At such times, the copper normality increased, the "free" CN^- normality decreased and the solution became blue. However, it was found that the use of an E.A.C. treatment at the maximum permissible cathode current density would bring the bath back to a stable condition. On the other hand, an unstable bath such as Bath 2 could not be changed into a stable bath by such treatment.

During the E.A.C. treatment of an unstable bath which originally had been stable, a thick, black, adherent coating is formed on the copper anodes, provided that the bath is slowly agitated. Copper then is plated on the cathode faster than it is dissolved at the anode and the "free" CN^- normality is increased. When the "free" CN^- and OH^- normalities again have become equal, the bath is again stable, the black coating ceases to be adherent and can be readily removed, and the bath is again colorless.

If a bath whose composition is outside the limits for stable baths is given an E.A.C. treatment, the result is different. The anodes become coated with a very adherent, black coating which can only be removed by a mechanical or chemical treatment. The bath remains unstable throughout this procedure.

DISCUSSION AND SUMMARY

In the earlier experiments performed during this research, it was shown that the compositions of typical copper cyanide

plating baths recommended in the past change during operation at 25C (77F), i.e., these baths are unstable.

We had previously discovered that stable zinc and cadmium cyanide plating baths can be produced, and that these remain stable only as long as a certain relationship exists between the OH⁻ normality and the total CN⁻ normality, the nature of this relationship being different in each case. We then explored the feasibility of producing stable copper cyanide plating baths at 25C and the possibility that there might be a relationship between the OH⁻ normality and total CN⁻ normality in such baths.

We have shown that stable copper cyanide baths can be produced. However, we found that the OH⁻ normality in such baths is related to the "free" CN⁻ normality rather than to the total CN⁻ normality.

Correctly-formulated copper cyanide plating baths must be subjected to a preliminary electrolysis before they can become stable, although this is not the case when plating in zinc and cadmium baths. A method of determining the original bath composition required to produce a stable bath of the required specification, is suggested.

Finally, when stable copper cyanide baths become temporarily unstable owing to the use of too high a cathode current density or of an improper ratio between anode area and cathode area, they can be brought back to the stable state by the use of an electrolytic activated carbon (E.A.C.) treatment. This same treatment can be used for increasing the purity of the plating bath after it has been produced from chemicals available on the market.

The remainder of the experimental work was devoted to a study of the results obtained when the stable copper cyanide baths were used in plating at 25C. It was found that the operating conditions of the cell and the nature and adhesion of the copper deposits obtained when using the stable Baths 3, 4 and 5 were much superior to those obtained with the unstable Baths 1 and 2. The new Bath 3 could well be used as a "strike" bath and the new Baths 4 and 5 could well be used for plating comparatively thick copper coatings on steel without the use of a "strike" bath.

Of special interest was the discovery that high strength Type 4037 steel can be plated with copper in any one of the stable copper cyanide baths referred to in this paper without becoming embrittled.

CONCLUSIONS

Present-day copper cyanide plating baths are unstable in use. However, new baths developed during this research are stable when used at 25C (77F). The compositions of these baths conform to the relationships:

- (1) OH⁻ normality = "free" CN⁻ normality
- (2) $\frac{\text{total NaCN normality}}{\text{Cu normality}}$ ratio varying between 2.6 and 2.9 depending on the concentration of the bath

These stable baths have a number of very important advantages which include:

- (1) comparatively simple control of the bath compositions, which would result in greater uniformity and higher quality in the plated products
- (2) improvement in the nature and adhesion of the copper deposits and in the plating cell operating conditions
- (3) ability to use higher cathode current densities
- (4) ability to copper plate high strength steel such as Type 4037 without embrittling the steel
- (5) ability to plate comparatively thick copper coatings directly on steel without the use of a "strike" bath

It is concluded, also, that the stable baths can become temporarily unstable due to the use of too high a cathode current density or of an incorrect ratio of anode area to cathode area. To rectify this, a method of renewing the stability of the bath is described, using an electrolytic activated carbon treatment. This treatment also can be used for increasing the purity of a bath when it is first made up.

Although the newly-developed baths are not stable when they are first made up, they become stable after a period of initial plating has taken place. The composition of the bath prior to this initial treatment, i.e., when it is first made up, may be determined by the following procedure:

- (1) Decide on the normality of copper cyanide required in the stable bath desired.
- (2) Using the curve in Fig. 3 of this paper, determine the total NaCN normality required by the copper cyanide concentration.
- (3) Using the curve in Fig. 4 of this paper, determine the "free" CN⁻ normality that will be present in the stable bath having the total NaCN concentration obtained in (2).
- (4) The NaOH normality required will be equal to the "free" CN⁻ normality.

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