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*IMPROVED SILVER CYANIDE
PLATING BATHS: LABORATORY
DEVELOPMENT*

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EXTRACTION METALLURGY DIVISION

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Improved Silver Cyanide Plating Baths: Laboratory Development

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

ABSTRACT

Improved silver plating results were obtained during laboratory experiments in which the bath constituents were related to one another as follows:

- (1) $Y = 0.374 + 0.768X - 0.178X^2$
where $Y = \text{OH}^-$ normality
and $X = \text{"free" CN}^-$ normality
- (2) $\frac{\text{total NaCN normality}}{\text{Ag normality}}$ is between 6.1 and 8.1
(the exact value depending on the bath composition)

The advantages of these improved silver plating baths include: low rate of cyanide consumption and carbonate formation; high current efficiency and low cell voltage when operating at comparatively high cathode current density; deposition of uniform fine-grained deposits in the absence of brighteners; insolubility of the silver anodes in the plating bath when the latter is not in use; absence of silver deposition on unconnected steel cathodes immersed in the plating bath; ability to plate satisfactory silver deposits directly on steel; ability to plate high strength steels, such as Types 1062 and 4037, directly with silver without embrittling the steels.

SILVER HAS ELECTRICAL, mechanical and chemical properties which have led to its use as a coating on many types of metal products. The literature shows that silver has been electrodeposited from a wide variety of electrolytes; however, most of the plating now is done in alkali cyanide-silver cyanide baths. Potassium compounds are commonly used in preference to sodium compounds in silver plating solutions because they are generally purer, the baths can be operated at higher current densities and they can tolerate more carbonate in solution.

Foulke and Diggin¹ have described present-day silver plating practice. According to these authors the most important chemicals required in producing the plating baths are silver cyanide (AgCN) and potassium cyanide (KCN), although potassium carbonate and potassium hydroxide are sometimes added. Also mentioned is the fact that sodium cyanide is rarely used except for some strike baths. They recommend the following three-stage plating process to obtain adhesion of the silver on steel: (1) plate in a copper-silver strike bath with a high "free" cyanide content (2) plate in a similar bath containing no copper and (3) plate in a more concentrated bath. Generally it is believed that the silver is present in the plating bath in the form of the complex ion $\text{Ag}(\text{CN})_2^-$. Any cyanide in the bath in addition to that required to form the compound $\text{KAg}(\text{CN})_2$ is termed "free" cyanide.

It is well known that carbonate forms in silver plating solutions and that, when above a certain limit, it has an adverse effect on the deposits and must be removed. It can be precipitated by chemical methods or, at least in the case of sodium cyanide baths, by cooling the solution to a temperature low enough to produce precipitation without the aid of additional chemicals.

According to Foulke and Diggin¹ hydroxide is used almost

exclusively in high speed silver plating baths for producing harder silver deposits. Greenspan² has stated that hydroxide is used to counteract the formation of undesirable decomposition products, thus increasing the stability, improving the deposit and assisting anode corrosion. He adds, however, that the role of hydroxide in the electrolyte has not been completely explained. Both of these authorities suggest a maximum hydroxide content of 30 g/l (0.54 normal).

In fairly recent papers³⁻⁵ the present authors described improved sodium cyanide baths for plating zinc, cadmium and copper. We showed that the relationship of the total cyanide to the hydroxide in the zinc and cadmium baths, and the relationship of the "free" cyanide to the hydroxide in the copper baths, is more important than the relationship of the total cyanide to the metal content. The improved baths which were recommended are stable and do not produce carbonates during electrolysis provided that they are not operated above their limiting cathode current densities. For each bath concentration the maximum cathode current density at which 100 per cent plating efficiency is obtained is substantially higher than that which can be used with ordinary commercial baths of similar concentration. Whereas high strength steels, such as those of Types 1062, 4037 and 4340, are severely embrittled when plated with zinc, cadmium or copper in typical commercial baths, these steels are not significantly embrittled when plated in laboratory-prepared baths of the improved type referred to above.

In view of these developments, it was felt that a similar improvement probably could be made in plating silver from sodium silver cyanide baths if the required relationships between total cyanide and silver normalities, and between "free" cyanide and hydroxide normalities, could be discovered. The present paper describes the experiments which led to the discovery of these relationships. The improved characteristics of the new types of bath produced in this way are also described.

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TABLE I
STEEL ANALYSIS (PER CENT)

Constituent	Type of Steel (AISI)	
	1062	4037
Carbon	0.64	0.40
Manganese	1.03	0.76
Silicon	0.16	0.31
Molybdenum	—	0.26
Sulfur (max)	<0.009	0.02
Phosphorus (max)	<0.002	<0.02

MATERIALS, EQUIPMENT AND PROCEDURES

Electrodes

The cathode materials used during this research were as follows:

- (1) Sheets cut from zinc-coated, low-carbon-steel Hull cell panels, to a size of 6.35 x 1.27 x 0.025 cm (2.5 x 0.5 x 0.01 in.). (The zinc coating was removed before the silver plating was begun.)
- (2) Type 1062 high-carbon-steel pins, 8.26 cm (3.25 in.) long and 0.38 cm (0.15 in.) in diameter. They had been produced from drawn wire and austempered in the bainitic range, resulting in a Rockwell C hardness of 52-56 and an ultimate strength of 18-19.6 kg/mm² (257-279 kpsi). They were covered with a thin uniform scale of blue iron oxide when received.
- (3) Type 4037 steel pins, 6.35 cm (2.5 in.) long and 0.40 cm (0.15 in.) in diameter. They had been produced from drawn wire and then quenched and tempered, resulting in a Rockwell C hardness of 51 to 55. When received they were covered with a thin, very porous film of copper that had been applied to prevent decarburization during heat treatment, and a black smut.

The analyses of the Types 1062 and 4037 steels are given in Table I.

The anodes used in the experiments were of bar silver specially produced for use in electroplating. The immersed portion of each one was 12.7 x 2.5 x 0.6 cm (5 x 1 x 0.2 in.).†

Cathode Surface Preparation Prior to Silver Plating

Before silver plating, each low carbon steel sheet cathode was treated as follows:

- (1) Stripped of zinc by immersion in 18 per cent (by weight) hydrochloric acid produced by diluting concentrated chemically pure acid with distilled water. This operation was performed at room temperature and was continued until vigorous gas evolution had ceased.
- (2) Rinsed thoroughly in tap water.
- (3) Introduced into the plating bath with as little delay as possible.

Each pin of Type 1062 steel was treated by a procedure recently developed in this laboratory,⁶ which produces a surface that is thoroughly clean, smooth, active, and free from embrittlement. This procedure was as follows:

- (1) Degreased in the vapor of suitably stabilized trichloroethylene.
- (2) Immersed in 18 per cent hydrochloric acid (by weight), 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* operating at 25 kc and 150 W.)
- (3) Rinsed in flowing tap water.

- (4) Immersed in a 10 per cent copper sulfate (CuSO₄ · 5H₂O) solution of pH 2.6.
- (5) Rinsed in flowing tap water.
- (6) Immersed in a solution containing nitric acid (7 per cent by weight) and acetic acid (14 per cent by weight) for 3-5 min. During this treatment the copper coating and other impurities on the steel surface were loosened or removed, and the roughness was eliminated.
- (7) Rinsed in water while under the influence of ultrasonic vibration. This treatment removed all smut and copper remaining on the surface from the previous treatment.
- (8) Introduced into the plating bath with as little delay as possible.

Each pin of Type 4037 steel was treated by a procedure consisting of steps 1, 6 and 7 of the treatment used with the Type 1062 pins. Steps 2 to 5 were not used, because these pins were copper-coated when received.

Electroplating

This operation was performed in a plating bath of 800 ml volume in a cylindrical glass container. Both vertical edges of the single flat silver anode were placed against one side of the container. Each sheet steel cathode, suspended by means of a silver-plated steel clip, was placed at an angle of 90 degrees to, and with its near edge 3.8 cm (1.5 in.) from, the anode. Under these circumstances the silver was plated on both sides of the cathode and it was dissolved on only one side

of the anode. The ratio $\frac{\text{effective anode area}}{\text{effective cathode area}}$ was 3.5.

When Type 1062 or Type 4037 pins were being plated a similar arrangement was used except that this ratio was 4.7 or 6.3 respectively.

The plating bath was agitated slowly by a Teflon-coated steel propeller. One series of cathodes was plated at a temperature of 25 ± 2C (77F) and a second one at 49 ± 2C (120F).

Each plating bath was prepared by dissolving reagent-grade chemicals in distilled water and adding activated carbon. The mixture then was electrolyzed, using a mild steel cathode and a silver anode, to remove soluble impurities. Finally the mixture was filtered through Whatman No. 52 paper to remove the carbon and any other solid particles that might be present. (This purification procedure had previously been developed in this laboratory.⁶)

During the actual plating experiments the volume of the bath was maintained constant. It was analyzed whenever advisable, using the procedure given in the Metal Finishing Guidebook.²

Coating Thickness Testing

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

Cathode Current Efficiencies

The cathode current efficiencies obtained with the various plating procedures were determined using a copper coulometer⁷ in the plating circuit.

Bend Testing of Steel Pins

A slow-bend test was used to determine the extent to which the pins had become embrittled during plating, and the quality of the adhesion of the electroplated silver to the basis metal. This test was performed in a Hounsfield notched-bar bending jig attached to a Type W tensometer machine equipped with a motor drive. The details of the test have

†Johnson, Matthey and Mallory Ltd.
*Branson Ultrasonic Corp.

TABLE II
PUBLISHED SILVER PLATING BATHS INVESTIGATED
IN THIS LABORATORY (NORMALITY)

Constituent	Bath 1 (copper-silver strike)	Bath 2 (conventional)	Bath 3 (high speed)
AgCN	0.014	0.27	0.67
CuCN	0.125	—	—
KCN	1.15	0.92	1.8
"Free" CN ⁻ *	0.8	0.49	0.85
KOH*	Trace	Trace	0.27
K ₂ CO ₃ **	Trace	0.24	0.22

*Determined after constituents were dissolved in solution.

**Depends on the purity of chemicals used.

been described.⁶ During the test, the steel pin was bent until it broke or until a bend of 135° had been produced. Pins that could be bent through this angle in 11 min without breaking were considered to have passed the embrittlement test.

EXPERIMENTAL

Improvement of Cyanide Silver Plating Baths

A study of the silver plating processes referred to in two well-known books in this field^{1, 2} revealed a considerable variation in the bath compositions recommended for the three-stage process of plating this metal on steel. Finally it was decided that a copper-silver cyanide strike bath, a conventional bath and a high speed bath recommended by Greenspan² (Baths 1, 2 and 3 in Table II) would be used in the preliminary laboratory experiments of the present research. Each bath was analyzed before and after plating. As shown in Table III, the composition of each of the three baths changed during plating, i.e., all of these baths are "unstable."*

*As used in this paper, "stable" baths do not change in composition on continued electrolysis, whereas "unstable" baths do. Loss by dragout is not considered to constitute such a change.

This was particularly obvious in the case of Bath 3 which was used at a high current density for a comparatively long time. The "unstable" chemical conditions which were revealed in these baths were similar to those which had been observed earlier in the standard commercial baths for plating zinc, cadmium and copper.

Experiments then were conducted with sodium cyanide silver plating baths containing various concentrations of hydroxide. After considerable experimentation, baths were discovered in which the composition did not change under suitable conditions of cathode current density, temperature and anode-to-cathode ratio. Typical examples of these were Baths 4 and 10 in Table III. Similar results also were obtained in these baths when the current densities were considerably higher (5.4 and 25.8 A/dm²) than those shown in the table. Eventually Baths 4 to 11, having the wide range of analyses shown in Table IV, were found to have compositions that did not change during plating.

During these experiments it was discovered that all aqueous solutions produced by dissolving various proportions of silver cyanide, sodium cyanide and sodium hydroxide, underwent a change in composition (i.e., were "unstable") when they first were electrolyzed at 25C (77F) using a silver anode and steel cathode. Eventually some of these ceased to change, i.e., they become "stable." The others continued to change indefinitely.

The baths which had become stable always had compositions which agreed with the following two equations:

$$Y = 0.374 + 0.768X - 0.178X^2 \quad (1)$$

where Y was the OH⁻ normality
and X was the "free" CN⁻ normality

(The curve corresponding to this equation is shown in Fig. 1.)

$$\frac{\text{Total NaCN normality}}{\text{Ag normality}} \text{ varied between 6.1 and 8.1.} \quad (2)$$

TABLE III
COMPARISON OF THE STABILITY OF TYPICAL PUBLISHED PLATING BATHS
(1, 2 AND 3) WITH THAT OF TYPICAL NEW BATHS (4 TO 10)

Bath No.	Plating Temperature (C)	Cathode Current Density (A/dm ²)	Length of Plating Time (hr)	Analysis (normality)				Bath Stability
				Ag	"Free" CN	OH	CO ₃	
1	25	1.6	0	0.01	0.80	Trace	Trace	Poor
2	25	2.2	0.2	0.02	0.63	0.03	-0.05	Poor
			1.7	0.26	0.49	Trace	0.24	
3	49	8.0	0	0.23	0.43	0.03	0.34	Poor
			9.0	0.70	0.85	0.27	0.22	
4	25	3.2	0	0.90	0.66	0.15	0.34	Good
			2.2	0.16	1.08	1.00	Trace	
10	25	10.8	0	0.16	1.08	1.00	Trace	Good
			3.0	0.40	2.20	1.20	0.18	
				0.40	2.20	1.20	0.18	

TABLE IV
ANALYSES OF NEW SODIUM CYANIDE SILVER PLATING BATHS (NORMALITY)

Constituent	Bath 4	Bath 5	Bath 6	Bath 7	Bath 8	Bath 9	Bath 10	Bath 11
AgCN	0.16	0.18	0.26	0.30	0.40	0.40	0.40	0.40
NaCN (total)	1.30	1.48	1.84	2.13	2.45	2.52	2.65	2.85
Na ₂ CO ₃ *	Trace	0.06	0.02	0.06	0.06	0.06	0.08	nd**
"Free" CN ⁻	1.08	1.28	1.40	1.70	2.00	2.10	2.20	2.40
NaOH	1.00	1.06	1.10	1.17	1.20	1.20	1.20	1.20

*Depends on the purity of the chemicals used.

**Not determined.

Note: Na₂CO₃, "free" CN⁻, and NaOH were determined after the bath had been electrolyzed until it reached the "stable" condition. The current density used did not exceed the limiting value for the particular bath at the temperature used.

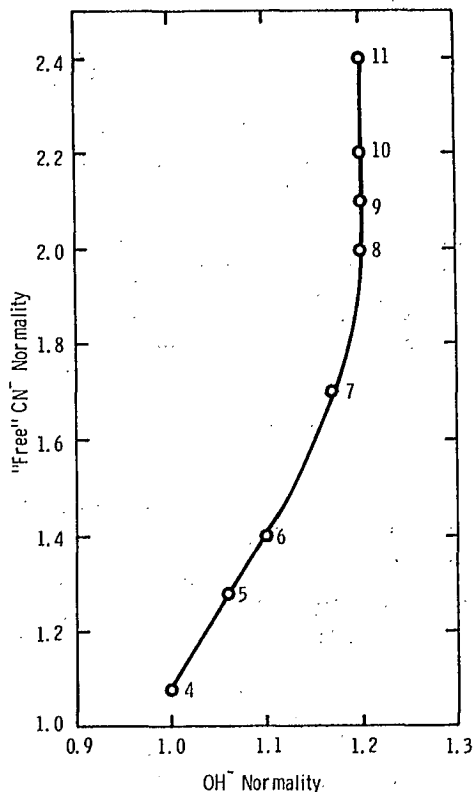


Fig. 1. Relationship between the "free" CN⁻ and OH⁻ normalities in new silver plating baths.

(The values obtained for Baths 4 to 11 were 8.1, 8.0, 7.7, 7.1, 6.1, 6.3, 6.6 and 7.1 respectively.)

The curve obtained when the total NaCN normality was plotted against the AgCN normality in Baths 4 to 11 is shown in Fig. 2. The baths which continued to change in composition during electrolysis appeared never to agree with the above equations.

Characteristics of the New Cyanide Silver Plating Baths

Effect of Cathode Current Density on the Stability

Plating was done on sheet cathodes of low-carbon steel in the "stable" baths 4 to 11, to determine the range of cathode current densities that would not produce instability in each

TABLE V
EFFECT OF CATHODE CURRENT DENSITY ON THE STABILITY OF TYPICAL NEWLY DEVELOPED BATHS AT 25C (77F)

Cathode Current Density (A/dm ²)	△—slightly unstable				φ—stable			
	Newly-Developed Baths							
	4	5	6	7	8	9	10	11
1.6	φ	φ	φ	φ	φ	φ	φ	φ
3.2	φ	φ	φ	φ	φ	φ	φ	φ
3.8	△	φ	φ	φ	φ	φ	φ	φ
5.4		φ	φ	φ	φ	φ	φ	φ
5.9		△	φ	φ	φ	φ	φ	φ
8.0			φ	φ	φ	φ	φ	φ
10.2			△	φ	φ	φ	φ	△
12.7				φ	φ	φ	φ	
12.9				△	φ	φ	φ	
16.1					φ	φ	△	
16.7					φ			
17.2					φ			
17.8					△			

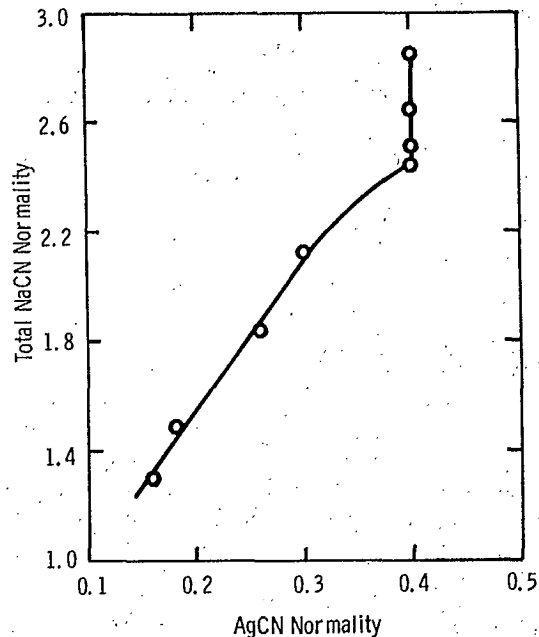


Fig. 2. Relationship between the normality of the AgCN and that of the total NaCN in the initial baths from which the new baths are produced.

bath. The results obtained at 25C (77F) are presented in Table V, and those obtained at 49C (120F) in Table VI. It is shown that at 25C all of these baths remained "stable" at current densities up to 3.2 A/dm², but only Bath 8 remained stable at a current density as high as 17.2 A/dm²; also that increasing the bath temperature to 49C (120F) increased the maximum current density at which each bath remained stable.

Effect of Cathode Current Density on the Cathode Current Efficiency

In these experiments the plating was done on sheet cathodes of low-carbon steel in baths 7, 9 and 10. It is shown in Table VII that the maximum cathode current density at which the cathode current efficiency was 100 per cent was greater for Bath 9 than for Baths 7 or 10, at both 25 and 49C. It also is shown that the current efficiency decreased fairly rapidly as soon as the maximum current density was exceeded. The maximum current density at which the current efficiency is 100 per cent has been found in this research to be much lower

TABLE VI
EFFECT OF CATHODE CURRENT DENSITY ON THE STABILITY OF TYPICAL NEWLY-DEVELOPED BATHS AT 49C (120F)

Cathode Current Density (A/dm ²)	△—slightly unstable				φ—stable			
	Newly-Developed Baths							
	4	5	6	7	8	9	10	
5.4	φ	φ	φ	φ	φ	φ	φ	φ
5.9	△	φ	φ	φ	φ	φ	φ	φ
11.8		φ	φ	φ	φ	φ	φ	φ
12.1		△	φ	φ	φ	φ	φ	φ
18.8			φ	φ	φ	φ	φ	φ
19.4			△	φ	φ	φ	φ	φ
20.5				φ	φ	φ	φ	φ
21.0				△	φ	φ	φ	φ
25.8					φ	φ	φ	φ
26.4					φ	φ	φ	△
26.9					φ	φ	φ	
27.4					△	△		

TABLE VII
EFFECT OF CATHODE CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY OF NEW AND PUBLISHED BATHS (PER CENT)

Cathode Current Density (A/dm ²)	(a) 25 ± 2C (77F)		(b) 49 ± 2C (120F)	
	Cathode Current Efficiency (per cent)			
	Published Bath	New Baths		
	3	7	9	10
8.0	100 } (b)			
10.8				
12.7		100 } (a)		
12.9				
15.4				100 } (a)
16.1			100 } (a)	
16.7			96.2 } (a)	
17.2				97 } (a)
20.5		100 } (b)		
20.6				
25.8				100 } (b)
26.4			100 } (b)	
26.9				96 } (b)
27.4			100 } (b)	96.2 } (b)

when plating in "unstable" potassium or sodium cyanide baths than when plating in the new improved sodium cyanide baths.

Other Observations

The silver deposited from these baths was uniform and fine-grained in the absence of brighteners.

The cell voltage remains relatively constant during plating. The anode is always bright and free from nonmetallic films. The anode dissolves only during plating.

Very little crystalline material accumulates on the anodes and cell walls regardless of the concentration of the bath.

Effect of Bath Composition on Embrittlement of Certain High-Strength Steels and on Adhesion of the Deposit

Pins of Types 1062 and 4037 high-strength steel were plated with silver in Baths 1, 2 and 3. Then they were tested for embrittlement and for adhesion of the silver to the steel. As shown in Table VIII, the properties of the plated pins from all three potassium cyanide baths were unsatisfactory. A large proportion of the pins from Bath 1 had become severely embrittled; Bath 2 produced poor adhesion; and Bath 3 yielded both severe embrittlement and poor adhesion. Similar results (not shown) were obtained when pins were plated in sodium cyanide baths that did not conform to the above relationships.

Similar high strength steel pins were plated with silver in sodium cyanide baths 4, 5, 6 and 8 under suitable conditions and then subjected to the above-mentioned tests. The results obtained are presented in Table VIII. It will be noted

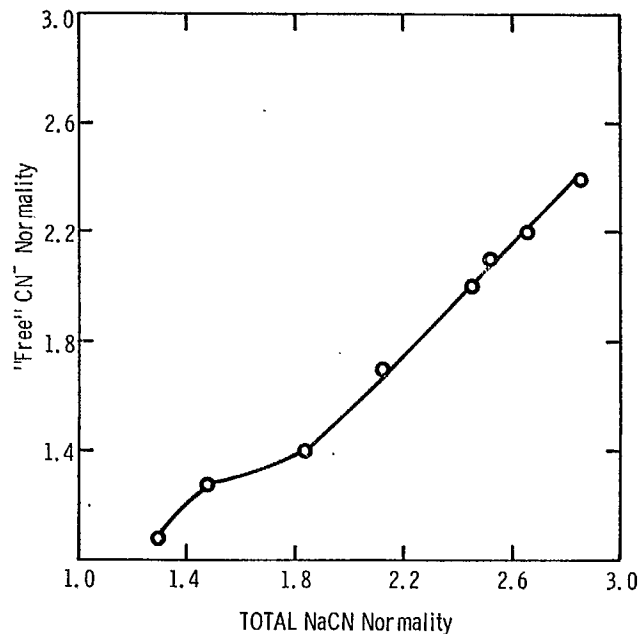


Fig. 3. Relationship between the normality of the total NaCN required in the initial bath and that of the "free" CN⁻ required in the final new bath.

that none of these plated pins broke when bent through an angle of 135 degrees, indicating that they all were free from significant embrittlement; and the adhesion of the silver to the pins was very good.

Results Obtained When the OH⁻ Normality Was Higher or Lower than that Required for a "Stable" Sodium Cyanide Bath
OH⁻ Normality Slightly Higher or Lower

When the OH⁻ normality of a sodium cyanide bath was slightly higher or lower than that required for a "stable" bath as outlined in Eq 1 above (say 1.2 g/l higher or lower), the limiting cathode current density was much lower than when the OH⁻ normality agreed exactly with this relationship. When used at or below these lower limiting current densities, the baths remained stable and had characteristics somewhat similar to those of the baths which exactly fulfilled both of the requirements for stability. However, serious deterioration of the bath occurred if the limiting current density was exceeded.

OH⁻ Normality Considerably Higher or Lower

Baths in which the OH⁻ normality was considerably higher than that required for stability were "unstable" at any cathode current density, and pins plated in them became highly embrittled. On the other hand, the adhesion of the

TABLE VIII
RESULTS OF SLOW BEND TESTS ON PLATED TYPES 1062 AND 4037 PINS

	Published Baths			New Baths			
	1	2	3	4	5	6	8
Plating Temp. ± 2C	25	25	49	49	49	49	49
Cathode Current Density (A/dm ²)	1.6	2.2	10.8	5.4	11.8	18.8	26.9
No. of Pins Bent	12	12	12	3*	24	12	12
No. of Pins Unbroken	2	12	4	3*	24	12	12
Angle of Bend Before Breaking (degrees)	58-132	>135	91-129	>135	>135	>135	>135
Adhesion to Steel	Good	Very poor	Very poor	Very good	Very good	Very good	Very good

*Type 1062 pins only.

TABLE IX
CONVERSION FACTORS

Ion or Compound	Equivalent of a One Normal Solution of the Ion or Compound	
	g/l	oz/gal
Ag ⁺	107.9	14.5
Cu ⁺	63.6	8.5
K ⁺	39.1	5.2
Free CN ⁻	26.0	3.5
OH ⁻	17.0	2.3
CO ₃ ⁻	30.0	4.0
Na ₂ CO ₃	53.0	7.0
NaCN	49.0	6.5
AgCN	133.9	17.9
KOH	56.1	7.5
K ₂ CO ₃	69.1	9.3

silver deposits from these baths was fairly good. The same was true of baths in which the OH⁻ normality was considerably lower than that required for stability, except that the adhesion of the deposits was very poor.

Procedure for Producing an Improved Sodium Cyanide Plating Bath Having a Certain Silver Cyanide Normality*

A method for determining the composition of an initially "unstable" bath which, after preliminary electrolysis, becomes a "stable" bath having the desired silver cyanide content, is as follows. (It will be recalled that the normalities of the silver and the OH⁻ ion do not change during the conversion of the original unstable bath into the final stable bath.)

- Decide the normality of silver cyanide required in the final stable silver plating bath.
- Determine the total NaCN normality required in the initial bath, using the silver cyanide normality referred to in (a) and the curve in Fig. 2.
- Determine the "free" CN⁻ normality required in the final stable bath, using the total NaCN normality required in the initial bath and the curve in Fig. 3.
- Determine the OH⁻ normality required in the initial bath, using the "free" CN⁻ normality required in the final bath and the curve in Fig. 1.

CONCLUSION

The following conclusions were drawn on the basis of the laboratory experiments described above:

- Improved sodium cyanide baths for electroplating silver have been developed on a laboratory scale. After preliminary treatment these remain unchanged in composition (i.e., they are "stable") under certain conditions of temperature, cathode current density and ratio of anode area to cathode area. The normalities of the constituents of these new "stable" baths are related as follows:

$$(a) Y = 0.374 + 0.768X - 0.178X^2 \quad (1)$$

where Y is the OH⁻ normality
and X is the "free" cyanide normality.

$$(b) \frac{\text{total NaCN normality}}{\text{Ag normality}} \text{ varies between 6.1 and 8.1} \quad (2)$$

depending on the bath concentration.

*For relation between normality, g/l, and oz/gal see Table IX.

It is noteworthy that the OH⁻ contents of these baths are considerably higher than those of baths which have been recommended previously.^{1, 2}

- The preliminary treatment referred to in (1) consists of adding activated carbon to the bath and electrolyzing. At first the composition of the bath changes but eventually it ceases to change, i.e., it becomes "stable." When electrolyzing a bath which does not conform to equations (a) and (b) the composition continues to change indefinitely, i.e., the bath is "unstable." (A method of calculating the original composition of a bath which becomes stable after the preliminary treatment is included in this paper.)
- The composition of each of the newly-developed silver plating baths will change when the cathode current density has become too high (i.e., the bath will become unstable). However, the composition can be adjusted in such a way that the bath becomes stable again.
- Advantages of using the above-mentioned improved silver plating baths are as follows:
 - cathode current efficiencies of 100 per cent can be obtained at higher cathode current densities
 - the anodes do not dissolve during periods when plating is not being done
 - salt accumulation at the liquid-air interfaces is very slight
 - adherent silver coatings can be electroplated directly on steel surfaces without the use of preliminary "strike" coatings since the silver does not deposit by chemical replacement
 - high strength steels, such as Types 1062 and 4037, can be plated with silver without becoming significantly embrittled.

It remains to be seen how well these new silver plating baths will perform on a large scale. Pilot plant tests are contemplated when suitable equipment becomes available.

More recent work by the authors has revealed that the characteristics of potassium cyanide baths for plating silver also are similarly improved by adding specific amounts of potassium hydroxide. The details of this work will be reported later.

ACKNOWLEDGMENT

We thank Mr. R. F. Pilgrim for determining the equation of the curve in Fig. 1.

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