

**CANADA**

**IMPROVEMENT OF CADMIUM  
PLATING BATH COMPOSITIONS**

**W. DINGLEY & J. BEDNAR**

**DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA**

**EXTRACTION METALLURGY DIVISION**

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# Improvement of Cadmium Plating Bath Compositions

W. Dingley and J. Bednar\*

## ABSTRACT

Cyanide cadmium plating baths have been developed which are superior to those which have been recommended by previous investigators. In these baths the OH normality is equal to the CN normality. The following two baths are typical of those considered to be most desirable:

	NaCN	NaOH	Cd	Ratio $\frac{\text{NaCN}}{\text{Cd}}$
	(g/l)	(g/l)	(g/l)	(g/l)
(1)	98.3	80.3	34.5	2.8
(2)	137.3	112.5	48.8	2.8

Important characteristics of these baths are compared with those of the baths recommended in the past.

## INTRODUCTION

A GREAT DEAL OF CADMIUM electroplating now is being done in industry. In view of the recent improvements in cyanide zinc plating baths recommended by the authors,<sup>1</sup> and since the chemistry of cadmium is similar to that of zinc to a certain extent, it was decided to investigate cyanide cadmium plating baths to determine whether they could be improved in a somewhat similar manner.

The available cadmium plating literature as far back as 1940 was surveyed, the bath compositions recommended by the various authors were placed in a table (Table I) and the OH normalities were plotted against the CN normalities on a graph (Fig. 1). It will be noted that some bath numbers occur twice in the figure, indicating in each case that the investigator had recommended a range of baths instead of one single bath. (Throughout this paper "NaCN" means "total cyanide reported as NaCN").

Some authors apparently had mentioned the nature and amount of the chemicals actually present in their plating baths, including sodium cyanide, sodium hydroxide and cadmium. Others mentioned only the chemicals which had been dissolved to produce their baths and did not include the sodium hydroxide produced according to the reaction  $2 \text{NaCN} + \text{CdO} + \text{H}_2\text{O} \rightarrow \text{Cd}(\text{CN})_2 + 2 \text{NaOH}$ . For the sake of uniformity the amount of sodium hydroxide present in each of the second group of baths was calculated on the assumption, verified in this laboratory, that about 0.7 g/l of sodium hydroxide was present in any new bath for every 1 g/l of cadmium present. Calculated sodium hydroxide contents are identified with an asterisk in Table I.

Inspection of Table I, and particularly of Fig. 1, showed that the OH normalities of the various baths previously recommended, were considerably less than the CN normalities of these baths. As shown in the present paper, the compositions of these baths were found to change during plating, i.e., the baths were unstable. Accordingly the present investigation consisted largely of a study of cadmium cyanide plating baths, containing larger proportions of sodium hydroxide than previously used, to determine their stability and their plating characteristics. Since the chemistry of the additives used in the cadmium plating industry is not widely known and since their usefulness varies a great deal, the baths investigated (with one exception) contained no additives.

## MATERIALS, EQUIPMENT AND PROCEDURES

During this research all of the cadmium plating was done on steel cathodes some of which were cylindrical pins of Type 1062 material, while the remainder were of cold rolled sheet of Type 1010 material. The pins were 0.4 cm (0.15 in.) in

diameter and varied in length between 5.7 and 8.3 cm (2.25 and 3.25 in.). They had been produced from drawn wire and had been austempered in the bainitic range resulting in a Rockwell C hardness of 52-56. When received in this laboratory they were covered with a thin uniform blue coating of iron oxide. The sheet cathodes were 5.1 cm (2.0 in.) square and 0.08 cm (0.03 in.) thick and were comparatively free from visible oxide.

## Cathode Surface Preparation

Prior to cadmium plating, the surfaces of all cathodes were treated as follows:

- (1) degreasing with suitably stabilized trichlorethylene in a Model DLLV-B laboratory vapor degreaser.\*
- (2) pickling at room temperature in 18 per cent (by weight) hydrochloric acid produced by diluting the concentrated (37 per cent) reagent acid with distilled water. The operation was performed in a glass container which had been placed between two ultrasonic transducers containing Sonogen Z elements\*\* operating at a frequency of 25 kc  $\pm$  3 per cent and a load of 135-140 ma. The transducers were submerged in water 15 cm (6 in.) apart. The pickling time was one minute, too long a time giving inferior results.
- (3) thorough rinsing in water and introduction into the plating bath with as little delay as possible.

## Electroplating

The electroplating was performed in two litres of bath in a rectangular glass container 12.7 cm (5.0 in.) wide by 19 cm (7.5 in.) long by 12.7 cm (5.0 in.) deep. A cadmium anode, cut from a commercial anode, was placed against each of the two narrow sides of the container, the immersed portion of each anode being 5 by 5 cm (1.9 by 1.9 in.). The cathode was centrally located between the two anodes at least 1.3 cm (0.5 in.) below the surface of the bath. The latter was maintained at 25  $\pm$  2C (77F) and was agitated slowly by a rotating teflon-coated steel propeller. The direct current electricity was supplied from a copper/copper oxide rectifier suitably equipped with controls and meters.

The plating baths were prepared from sodium cyanide (NaCN), sodium hydroxide (NaOH), and cadmium oxide (CdO) of reagent quality, distilled water being the solvent. They were filtered through Whatman No. 52 filter paper to remove foreign particles when required. Additional distilled water was used to compensate for losses due to evaporation. Each bath was analyzed frequently to detect changes in composition, the procedures in the Metal Finishing Guidebook<sup>11</sup> being used.

\*Corrosion Section, Extraction Metallurgy Division, Department of Mines and Technical Surveys, Ottawa, Canada.  
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\*Manufactured by Canadian Hanson and Van Winkle Co., Toronto, Canada.  
\*\*Manufactured by Branson Ultrasonic Corp., Stamford, Conn., U.S.A.

### Coating Thickness Testing

The thicknesses of the electroplated cadmium coatings were determined by means of the Aminco-Brenner Magne Gage and by a stripping method. The latter consisted of weighing the plated sample ( $W_1$ ) on an analytical balance and then immersing it in 29 per cent (by weight) hydrochloric acid. It was left in the acid until the coating was completely stripped (as indicated by a sudden reduction in hydrogen evolution) after which it was thoroughly rinsed and rapidly dried in a hot air stream. It was allowed to cool to room temperature and then reweighed ( $W_2$ ). The coating thickness was calculated from the coating weight ( $W_1 - W_2$ ).

### EXPERIMENTAL WORK

#### Stability of Plating Baths

Determinations were made of the stabilities of a number of cadmium plating baths (Bath Nos. 11, 17, 21, 12, arranged in order of increasing concentration, and referred to in Table I and Fig. 1), typical of those which had been used by previous investigators. The procedure used was as follows. Each one was electrolyzed at 25C (77F) using cadmium anodes, square sheet or pin cathodes and a cathode current density of 4.1 amp/dm<sup>2</sup> (38 amp/ft<sup>2</sup>). A sample of each bath was removed periodically for analysis for sodium cyanide, sodium hydroxide, cadmium and carbonate and, at the same time, the cadmium-coated cathode was replaced by a new one. This was repeated a number of times. Analytical results showing that the compositions of these baths changed materially during the plating, i.e., that the baths had poor stability, are given in Table II. It may be added that the carbonate content of the baths was changed substantially also although the analytical results are not included in the table.

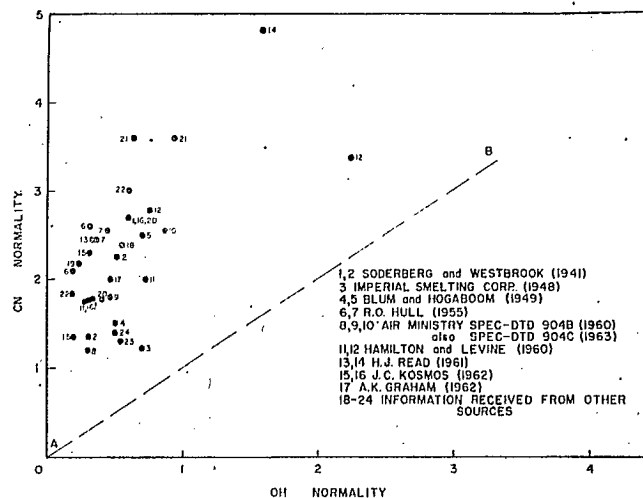


Fig. 1. Cyanide and hydroxide normalities of typical cadmium plating baths referred to by investigators since 1940.

After a considerable number of similar plating experiments had been performed using higher OH contents in the bath, it was found that baths in which the OH normality is equal to the CN normality are quite stable. This is shown by the data for three typical baths (Bath Nos. 25, 26, 27) which are given in Table II. These stable baths are on the line AB, which is shown in Figs. 1 and 2 and which has the equation

$$\text{OH normality} = \text{CN normality.}$$

As illustrated in Table III, baths having an OH normality greater than their CN normality also are unstable. The

TABLE I  
ANALYSES OF TYPICAL CYANIDE CADMIUM PLATING BATHS  
USED BY PREVIOUS INVESTIGATORS

		Bath Analyses					
		NaCN		NaOH		Cd	
Bath No. in Fig. 1		Grams/litre	Normality	Grams/litre	Normality	Grams/litre	Normality
G. Soderberg and L. R. Westbrook <sup>2</sup> (1941)	1	86.3-133.3	1.8-2.7	13.3-24.0*	0.3-0.6	18.8-33.8	0.4-0.6
	2	66.0-112.5	1.4-2.3	12.3-20.3*	0.3-0.5	17.3-28.5	0.3-0.5
Imperial Smelting Corporation <sup>3</sup> (1948)	3	60.0	1.2	27.8*	0.7	39.0	0.7
W. Blum and G. B. Hogaboom <sup>4</sup> (1949)	4	72.8	1.5	20.3	0.5	28.1	0.5
	5	120.0	2.5	27.8*	0.7	39.0	0.7
R. O. Hull <sup>5</sup> (1955)	6	112.5-127.5	2.1-2.6	7.5-11.3	0.2-0.3	15.0-20.3	0.3-0.4
	7	120.0-135.0	2.5-2.6	14.3-17.7*	0.35-0.45	20.3-24.8	0.35-0.45
British Air Ministry <sup>6</sup> (1960)	8	57.8	1.2	12.0*	0.3	17.0	0.3
Spec. DTD904B (1960)	9	87.8	1.8	18.4*	0.5	25.8	0.5
Spec. DTD904C (1963)	10	125.3	2.6	30.8	0.8	22.5	0.4
F. Hamilton and M. Levine <sup>7</sup> (1960)	11	85.5-96.0	1.8-2.0	11.3-29.3	0.3-0.7	20.3-33.0	0.4-0.6
	12	135.0-165.0	2.8-3.4	30.0-90.0	0.8-2.3	78.8-114.0	1.4-2.1
H. J. Read <sup>8</sup> (1961)	13	120.0	2.5	13.3*	0.3	18.8	0.4
	14	236.3	4.8	64.2*	1.6	90.0	1.6
J. C. Kosmos <sup>9</sup> (1962)	15	66.0-112.5	1.4-2.3	7.5-11.3	0.2-0.3	17.3-28.5	0.3-0.5
	16	86.3-133.3	1.8-2.7	12.3-23.6*	0.3-0.6	19.5-33.0	0.4-0.6
A. K. Graham <sup>10</sup> (1962)	17	98.3	2.0	18.8*	0.5	26.3	0.5
Information received from other sources (1956)	18	117.0	2.4	21.0	0.6	30.0	0.5
	19	106.5	2.2	9.0	0.2	20.3	0.4
	20	86.3-133.3	1.8-2.7	15.8-24.0	0.4-0.6	22.5-33.8	0.4-0.6
	21	176.3	3.6	26.3-37.5	0.7-0.9	48.8-56.2	0.9-1.0
	22	90.0-150.0	1.8-3.0	7.5-24.0	0.2-0.6	18.0-36.0	0.3-0.6
	23	63.8	1.3	21.8	0.5	29.3	0.5
	24	67.5	1.4	19.5	0.5	28.1	0.5

\*NaOH was not specified in these formulas, the figures given were calculated.

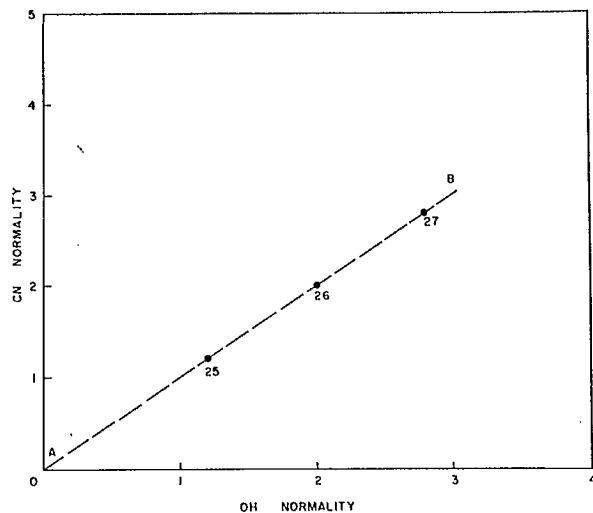
**TABLE II**  
**STABILITY OF TYPICAL PLATING BATHS INVESTIGATED**  
(cathode current density = 4.1 amp/dm<sup>2</sup>)

Bath No. in Fig. 1	Nature of Cathodes	Length of Plating Time (min)	Bath Analysis (g/l)			Bath Stability
			NaCN	NaOH	Cd	
11	sheet	0	84.0	18.8	21.8	poor
		360	79.5	13.5	23.3	
		780	72.8	9.0	29.3	
17	pins	0	97.5	21.8	28.5	poor
		300	86.3	16.5	27.0	
21	sheet	0	167.3	36.8	52.5	poor
		360	158.3	32.3	44.3	
		720	146.3	29.3	44.3	
12	sheet	0	180.0	88.5	108.0	poor
		420	169.5	77.3	103.5	
		780	164.3	70.5	108.0	
25	sheet	0	57.8	44.3	21.0	good
		360	57.8	44.3	21.0	
26	sheet	0	98.3	80.3	34.5	good
		240	98.3	80.3	34.5	
27	sheet	0	137.3	112.5	48.8	good
		300	137.3	112.5	48.8	

bath for which data are given in the table was 2.00 normal in NaCN, 2.25 normal in NaOH and 0.63 normal in Cd to begin with. Although it is not shown in the table, the carbonate content of this bath increased rapidly also.

**Effect of Cathode Current Density on Bath Stability**

The effect of increasing the cathode current density on the rate of change of the plating bath composition is shown in Table IV. Here a solution as nearly similar as possible to Bath No. 12 (referred to in Table I and Fig. 1) was electrolyzed at 25C (77F) and a cathode current density of 4.1 amp/dm<sup>2</sup> (38 amp/ft<sup>2</sup>). (Few present-day cadmium platers use a current density higher than 5.4 amp/dm<sup>2</sup>). A somewhat similar solution was electrolyzed at the same temperature and a cathode current density of 10.7 amp/dm<sup>2</sup> (100 amp/ft<sup>2</sup>). Although the second electrolysis lasted only 1/18 as long as the first one, the changes in the concentrations of sodium cyanide and sodium hydroxide were much greater. Pins were used as cathodes in these experiments.



**Fig. 2.** Cyanide and hydroxide normalities of stable cadmium plating baths.

The effects of increasing the cathode current density on the stabilities of Bath Nos. 11, 17, 21, 12 (recommended by previous investigators) are compared with those on the stabilities of Bath Nos. 25, 26, 27 (which were developed during this research) in Table V. Here it is shown that baths typical of those recommended by previous investigators are unstable even at a current density of 4.1 amp/dm<sup>2</sup> (38 amp/ft<sup>2</sup>). On the other hand, baths developed in the present research are stable at much higher current densities. Bath No. 25, which is comparatively dilute, is stable at 8.2 amp/dm<sup>2</sup> (76 amp/ft<sup>2</sup>) but unstable at 10.7 amp/dm<sup>2</sup> (100 amp/ft<sup>2</sup>). Bath Nos. 26 and 27, which are more highly concentrated, are stable at current densities as high as 19.4 amp/dm<sup>2</sup> (180 amp/ft<sup>2</sup>) and perhaps higher. These particular experiments were done with pins as cathodes.

**Other Bath Characteristics**

In Table VI it is shown that the plating cell voltage is unstable in the case of baths recommended by previous investigators such as Bath Nos. 11, 17, 21, 12, but is steady in the case of the newly developed baths (Nos. 25, 26, 27). The unstable voltages in the case of the former baths probably are due to the dark nonmetallic films that are formed on the surfaces of the anodes during plating, as indicated in the table. These films would be expected to increase the voltage drop and decrease the efficiency of metal solution at the anodes. In the case of the newly developed baths (Nos. 25, 26, 27)

**TABLE III**  
**STABILITY OF A CADMIUM PLATING BATH**  
**WHOSE OH NORMALITY IS GREATER**  
**THAN ITS CN NORMALITY**

Length of Plating Time (min)	NaCN (g/l)	NaOH (g/l)	Cd (g/l)
0	98.0	90.0	35.0
120	95.2	91.5	37.8
240	92.2	91.5	37.5
300	89.0	93.0	39.3

TABLE IV  
EFFECT OF INCREASING THE CATHODE CURRENT DENSITY ON STABILITY OF THE PLATING BATH

Cathode Current Density (amp/dm <sup>2</sup> )	Length of Plating Time (min)	Bath Analysis (g/l)		
		NaCN	NaOH	Cd
4.1	0	186.0	84.8	108.0
	360	185.3	81.0	106.5
10.7	0	189.8	92.3	103.5
	20	177.8	78.0	103.5

such compounds are not formed at the anodes so that the efficiency of the anode process would be greater.

The fact that there was more gassing at the cathodes when Bath Nos. 11, 17, 21, 12 were electrolyzed than when Bath Nos. 25, 26, 27 were treated in that way, indicates that the efficiency of cadmium deposition is greater in the case of the newly developed baths.

The appearance of the cadmium coatings produced in Bath Nos. 26, 27 was slightly more attractive than that of the coatings produced in Bath No. 25, and considerably more attractive than in the case of the previously recommended baths.

Although no actual throwing power measurements were made during this research, it was obvious from the inspection of the various cathodes that the covering abilities of Bath Nos. 25, 26, 27 were superior to those of Bath Nos. 11, 17, 21, 12.

In a few experiments with baths in which the OH normality was greater than the CN normality, it was found that the cell voltage tended to decrease on electrolysis and a dark nonmetallic film was formed on the anode. The cadmium coatings produced were as attractive-looking as those from Bath Nos. 25, 26, 27 except that the crystals were larger. The covering ability was less than that of Bath Nos. 25, 26, 27, but superior to that of Bath Nos. 11, 17, 21, 12.

In Bath No. 27 a coating thickness of 0.0003 in. was produced in one minute at a cathode current density of 19.4 amp/dm<sup>2</sup> (180 amp/ft<sup>2</sup>). It is important to note that a cooling system might be required in the bath when using such a high current density.

Cathode current efficiencies of between 85 and 98 per cent have been reported by previous investigators; however, these were obtained when the cathode current density was below 5.4 amp/dm<sup>2</sup> (50 amp/ft<sup>2</sup>). During the present research a current efficiency of 99 per cent was obtained at a current density of 4.1 amp/dm<sup>2</sup> (38 amp/ft<sup>2</sup>) and a current efficiency of 88 per cent was obtained at a current density of 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>).

All of the "other bath characteristics," except the coating

TABLE V  
STABILITY OF PREVIOUSLY RECOMMENDED BATHS COMPARED TO THAT OF THE NEWLY DEVELOPED BATHS AT DIFFERENT CURRENT DENSITIES

Cathode Current Density (amp/dm <sup>2</sup> )	Plating Baths						
	Previous Baths				Newly Developed Baths		
	11	17	21	12	25	26	27
4.1	X	X	X	X	φ	φ	φ
5.3						φ	
8.2					φ		φ
10.7				X	X		
11.8						φ	
12.9						φ	φ
16.0							φ
19.4						φ	φ

X—considerable deterioration.  
φ—no deterioration.

thickness, were determined on sheet steel panels. Pins were used in the coating thickness experiments.

#### Brightening Experiments

Although almost all of the work that has been described in this paper was done with baths that did not contain brighteners, a few words should be said regarding the brightening of some of the cadmium coatings obtained:

- (1) A standard brightener was added to Bath No. 26 and a number of pins were plated at 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>). The plated pins were very bright in appearance. Above this current density the results were less attractive.
- (2) Pins which had been plated at 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>) in Bath No. 26 (not containing brightener) were immersed in a solution containing 2.5 per cent of nitric acid and 0.5 per cent of hydrochloric acid (by weight) for two minutes and then thoroughly rinsed and dried. The surfaces of the pins were quite bright and attractive in appearance. The loss of metal was negligible.

#### DISCUSSION

It is of interest to note that the stable baths investigated

(Nos. 25, 26, 27) have had a  $\frac{\text{NaCN g/l}}{\text{Cd g/l}}$  ratio of about 2.8.

On the other hand, the values of this ratio in the case of the baths recommended by other investigators have varied between 1.4 and 6.3.

TABLE VI  
CHARACTERISTICS OF TYPICAL PLATING BATHS DURING ELECTROLYSIS (cathode current density = 4.1 amp/dm<sup>2</sup>)

	Bath 11	Baths 17 and 21	Bath 12	Bath 25	Baths 26 and 27
Cell Voltage	unstable	unstable	unstable	steady	steady
Anode appearance	very dark	very dark	very dark	bright metallic	bright metallic
Cathode gassing	slight at first and slowly increasing	slight at first and rapidly increasing	considerable	none visible	none visible
Cadmium coating appearance	slightly grey; large crystals	metallic white; crystals tiny at first then larger	metallic white; large crystals	slightly grey; tiny crystals	metallic white; tiny crystals
Covering ability	fair at first, becoming poorer	poor	fair	good	good

The authors found that the nature of the plating bath deterioration varied with the position of the bath in Fig. 1 or 2. When a bath on the left side of the line

OH normality = CN normality

was electrolyzed under electroplating conditions, its composition followed a line approximately parallel to this line, both OH and CN contents decreasing. On the other hand, when a bath on the right side of the line

OH normality = CN normality

was electrolyzed, its composition followed a line approximately perpendicular to this line, the OH content increasing and the CN content decreasing.

### CONCLUSIONS

On the basis of the experimental work described in this paper it is concluded that—

- (1) The cadmium cyanide electroplating baths recommended by earlier investigators (which have OH normalities less than their CN normalities):
  - (a) change in composition during plating and their instabilities increase greatly as the cathode current density is increased;
  - (b) have a metal solution efficiency at the anodes of well below 100 per cent as shown by the formation of a non-metallic film on the anode surfaces; and
  - (c) produce on the cathodes comparatively coarse crystalline cadmium deposits, which have a comparatively poor covering ability.
- (2) Cadmium cyanide baths whose OH normalities are equal to their CN normalities:
  - (a) are stable under normal plating conditions, and some of them are stable at cathode current densities much higher than normal;
  - (b) have higher cathode current efficiencies for a given cathode current density than is the case with baths having OH normalities less than their CN normalities;
  - (c) have a considerably improved metal solution efficiency at the anodes as shown by the absence of nonmetallic films on the surfaces, and by the maintenance of a constant cadmium content in the bath;
  - (d) produce much finer crystalline deposits of cadmium on the cathodes, which have a much improved covering ability; and
  - (e) produce deposits that can be brightened satisfactorily by a dilute acid treatment, or produce bright deposits when they contain suitable additives.
- (3) Cadmium cyanide baths whose OH normalities are greater than their CN normalities are unstable.

### REFERENCES

1. W. Dingley and J. Bednar, *Tech. Proc. Amer. Electroplaters' Soc.*, 50, 71 (1963).
2. G. Soderberg and L. R. Westbrook, *Trans. Electrochem. Soc.*, 80, 429 (1941).
3. "Zinc and Cadmium Plating," Imperial Smelting Corp., Ltd., 37 Dover St., London, W. 1, England. A Research Department Bulletin 1st ed. pp. 33-39 (1948).
4. W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming*, McGraw-Hill Book Co. Inc., New York, 3rd ed., pp. 315-318 (1949).
5. *Metal Finishing Guidebook*, 23rd Annual Edition (1955), Metals and Plastics Publications Inc., Westwood, New Jersey. Article by R. O. Hull (Cyanide Cadmium Plating), pp. 236-239.
6. British Ministry of Aviation Spec.—D.T.D. 904B (1960) and D.T.D. 904C (1963), Printed for Her Majesty's Stationery Office by Willsons (Printers) Ltd., Leicester, England.
7. W. F. Hamilton and M. Levine, *Tech. Proc. Amer. Electroplaters' Soc.*, 47, 160 (1960).
8. Hydrogen Embrittlement in Metal Finishing, H. J. Read, editor, Reinhold Publishing Corp., New York (1961). Chap. 6, article by N. M. Geyer, G. W. Lawless and Bennie Cohen, pp. 109-134.
9. *Metal Finishing Guidebook*, 30th Annual Edition (1962), Metals and Plastics Publications Inc., Westwood, New Jersey. Article by J. Kosmos (Cadmium Plating), pp. 268-270.

10. *Electroplating Engineering Handbook*, A. K. Graham, editor, Reinhold Publishing Corp., New York, 2nd ed. (1962), p. 239.
11. *Metal Finishing Guidebook*, 29th Annual Edition (1961), Metals and Plastics Publications Inc., Westwood, New Jersey.



WILFRED DINGLEY is a technologist at the Mines Branch Laboratories of the Department of Mines and Technical Surveys, Ottawa, Canada, where he has been actively engaged in the study of corrosion and its prevention for 18 years. During that period he has investigated a wide variety of problems submitted by government departments and industries. He is author or co-author of a number of published papers. He is chairman of the Metallic Coatings Subcommittee and a member of several other related committees of the Canadian Government Specifications Board.

JOHN BEDNAR is a technologist at the Mines Branch Laboratories of the Department of Mines and Technical Surveys, Ottawa, Canada, where he has worked in the field of corrosion and its prevention for the past five years. He has studied at the Free Ukrainian and Munich Universities in Munich, Germany; also at Carleton and Ottawa Universities in Ottawa, Canada.



### DISCUSSIONS

E. B. SAUBESTRE (Enthone Inc., New Haven, Conn.): In zinc plating, the importance of high hydroxide content is undoubtedly related to formation of the zincate ion, from which plating occurs. But are there comparable "cadmate" complexes? How do you account for the importance of hydroxide in the cadmium bath?

MR. DINGLEY: We add sodium hydroxide to the other constituents when making up a new bath. However, we have no evidence as to the nature of the ions which are present in the bath during plating.

R. SCOTT MODJESKA (Cinch Manufacturing Company, Chicago, Ill.): Did you have any observations with respect to the differences in adhesion of the deposits from this high alkaline bath as compared to those from conventional low alkaline baths?

MR. DINGLEY: Although we have not made a thorough study of the adhesion of our cadmium deposits we believe it to be at least as good as that of deposits from conventional baths.

DR. WILLIAM BLUM (Washington, D. C.): This question may seem unnecessary, in view of the high cathode efficiencies which you report. You assume that there is little, if any, hydrogen evolved or absorbed by the steel. Did you make tests with these high-carbon steels to show that there was less embrittlement of the steel when there was at most a small amount of hydrogen evolved?

MR. DINGLEY: We feel that the situation is somewhat more complicated than Dr. Blum's question would suggest. We believe we have evidence to show that hydrogen embrittlement may be due either to improper surface treatment prior to plating (for instance, pickling), or to hydrogen which enters the steel during plating.

In our experiments with the plating of Type 1062 steel with either zinc or cadmium, we at first had a great deal of difficulty with hydrogen embrittlement. However, we finally adopted a special pickling procedure and a special plating procedure which together gave us plated samples which were free from embrittlement on the basis of 90° bend tests. When we used conventional pickling and the special plating procedure, or the special pickling procedure and conventional plating, we again had trouble with embrittlement.

TABLE IV  
EFFECT OF INCREASING THE CATHODE  
CURRENT DENSITY ON STABILITY  
OF THE PLATING BATH

Cathode Current Density (amp/dm <sup>2</sup> )	Length of Plating Time (min)	Bath Analysis (g/l)		
		NaCN	NaOH	Cd
4.1	0	186.0	84.8	108.0
	360	185.3	81.0	106.5
10.7	0	189.8	92.3	103.5
	20	177.8	78.0	103.5

such compounds are not formed at the anodes so that the efficiency of the anode process would be greater.

The fact that there was more gassing at the cathodes when Bath Nos. 11, 17, 21, 12 were electrolyzed than when Bath Nos. 25, 26, 27 were treated in that way, indicates that the efficiency of cadmium deposition is greater in the case of the newly developed baths.

The appearance of the cadmium coatings produced in Bath Nos. 26, 27 was slightly more attractive than that of the coatings produced in Bath No. 25, and considerably more attractive than in the case of the previously recommended baths.

Although no actual throwing power measurements were made during this research, it was obvious from the inspection of the various cathodes that the covering abilities of Bath Nos. 25, 26, 27 were superior to those of Bath Nos. 11, 17, 21, 12.

In a few experiments with baths in which the OH normality was greater than the CN normality, it was found that the cell voltage tended to decrease on electrolysis and a dark nonmetallic film was formed on the anode. The cadmium coatings produced were as attractive-looking as those from Bath Nos. 25, 26, 27 except that the crystals were larger. The covering ability was less than that of Bath Nos. 25, 26, 27, but superior to that of Bath Nos. 11, 17, 21, 12.

In Bath No. 27 a coating thickness of 0.0003 in. was produced in one minute at a cathode current density of 19.4 amp/dm<sup>2</sup> (180 amp/ft<sup>2</sup>). It is important to note that a cooling system might be required in the bath when using such a high current density.

Cathode current efficiencies of between 85 and 98 per cent have been reported by previous investigators; however, these were obtained when the cathode current density was below 5.4 amp/dm<sup>2</sup> (50 amp/ft<sup>2</sup>). During the present research a current efficiency of 99 per cent was obtained at a current density of 4.1 amp/dm<sup>2</sup> (38 amp/ft<sup>2</sup>) and a current efficiency of 88 per cent was obtained at a current density of 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>).

All of the "other bath characteristics," except the coating

TABLE V  
STABILITY OF PREVIOUSLY RECOMMENDED  
BATHS COMPARED TO THAT OF THE NEWLY  
DEVELOPED BATHS AT DIFFERENT  
CURRENT DENSITIES  
Plating Baths

Cathode Current Density (amp/dm <sup>2</sup> )	Previous Baths				Newly Developed Baths		
	11	17	21	12	25	26	27
4.1	X	X	X	X	φ	φ	φ
5.3						φ	
8.2					φ		φ
10.7				X	X		
11.8						φ	
12.9						φ	φ
16.0							φ
19.4						φ	φ

X—considerable deterioration.  
φ—no deterioration.

thickness, were determined on sheet steel panels. Pins were used in the coating thickness experiments.

#### Brightening Experiments

Although almost all of the work that has been described in this paper was done with baths that did not contain brighteners, a few words should be said regarding the brightening of some of the cadmium coatings obtained:

- (1) A standard brightener was added to Bath No. 26 and a number of pins were plated at 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>). The plated pins were very bright in appearance. Above this current density the results were less attractive.
- (2) Pins which had been plated at 12.9 amp/dm<sup>2</sup> (120 amp/ft<sup>2</sup>) in Bath No. 26 (not containing brightener) were immersed in a solution containing 2.5 per cent of nitric acid and 0.5 per cent of hydrochloric acid (by weight) for two minutes and then thoroughly rinsed and dried. The surfaces of the pins were quite bright and attractive in appearance. The loss of metal was negligible.

#### DISCUSSION

It is of interest to note that the stable baths investigated

(Nos. 25, 26, 27) have had a  $\frac{\text{NaCN g/l}}{\text{Cd g/l}}$  ratio of about 2.8.

On the other hand, the values of this ratio in the case of the baths recommended by other investigators have varied between 1.4 and 6.3.

TABLE VI  
CHARACTERISTICS OF TYPICAL PLATING BATHS DURING ELECTROLYSIS  
(cathode current density = 4.1 amp/dm<sup>2</sup>)

	Bath 11	Baths 17 and 21	Bath 12	Bath 25	Baths 26 and 27
Cell Voltage . . . . .	unstable	unstable	unstable	steady	steady
Anode appearance . . . . .	very dark	very dark	very dark	bright metallic	bright metallic
Cathode gassing . . . . .	slight at first and slowly increasing	slight at first and rapidly increasing	considerable	none visible	none visible
Cadmium coating appearance . . . . .	slightly grey; large crystals	metallic white; crystals tiny at first then larger	metallic white; large crystals	slightly grey; tiny crystals	metallic white; tiny crystals
Covering ability . . . . .	fair at first, becoming poorer	poor	fair	good	good



