

Cyanide Formation in an Alkaline Noncyanide Zinc Plating Bath

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Zinc cyanide plating is most commonly used to prevent corrosion of steel products. It is easy to operate and to obtain a good zinc coating. A zincate bath or an acid zinc plating bath can also be used because the zinc cyanide bath is highly toxic, creates pollution, has work-safety problems, and there are strict laws regarding its wastewater.

A zincate bath without cyanide compounds has the following advantages: (1) the plating bath is nontoxic and allows easier wastewater treatment and a better work environment; (2) the bath composition is simple and easy to control; (3) the metal concentration is low and requires neutralization only for the removal of zinc by sedimentation; and (4) it does not need the decomposition of cyanide compounds in wastewater.

However, total cyanide is often detected in the wastewater of zincate bath shops. Some reports have shown that the cyanide ion is detected in wastewater and waste from various factories that do not handle any cyanide compounds.¹⁻⁶ This article reports on the formation of cyanide ion in the zincate bath.

To elucidate the detection of cyanide, the plating process and the wastewater treatment process in the zincate bath shops were investigated, and the total cyanide was determined using three standardized reference methods.

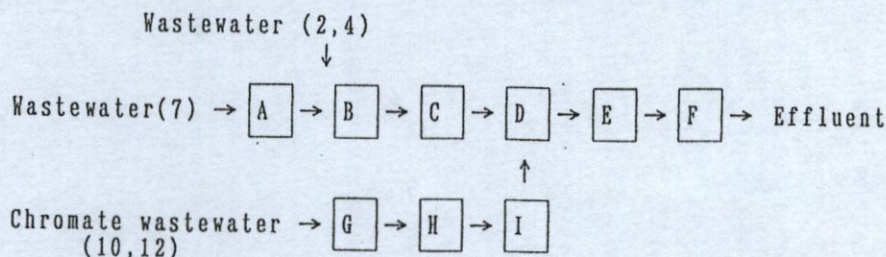


Figure 2. Wastewater treatment process: (A) reservoir tank 1, (B) reservoir tank, (C) pH adjustment tank, (D) sedimentation tank, (E) filter press, (F) final pH adjustment tank, (G) chromate reservoir tank, (H) reducing tank, (I) neutralization tank.

EXPERIMENTAL

Apparatus and Reagents

The same distillation equipment and reagents required by International Standardization Organization (ISO) methods,⁷ the standard methods text from the United States of America (SM),⁸ and Japanese Industrial Standard (JIS)⁹ were employed for the separation of total cyanide. All chemicals used were of the highest grade commercially available. The samples of zincate bath solutions, nitric acid dipping solutions, and effluents were obtained from five zincate bath shops.

Procedure

The total cyanide determination procedure is based on the ISO, SM, and JIS methods. To investigate the formation of hydrogen cyanide, an adequate amount of the sample was added to the

solution (~250 ml) for distillation together with the reagents and acid described in the three standardized reference methods. Distillation was carried out at a rather high temperature (>100°C) and in a highly acidic solution (<pH 2). The cyanide ion in the distillate was determined by the 4-pyridine carboxylic acid-pyrazolone methods.⁹ The nitrite ion in the nitric acid dipping bath and effluent were determined by the naphthylethylenediamine method.⁹

RESULTS AND DISCUSSION

Investigation of Zincate Bath Shops

The plating process and wastewater treatment process are shown in Figures 1 and 2. The numbers in the figures represent the locations of the samples in the shop. Analytical results of the

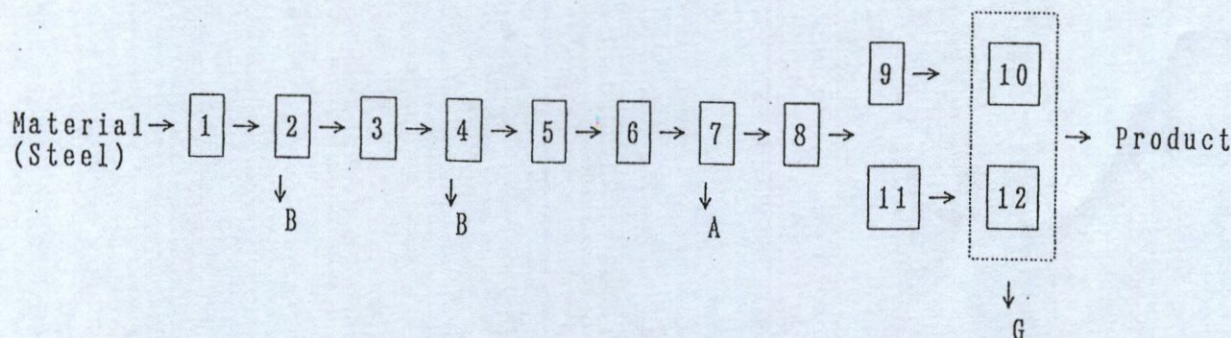


Figure 1. Plating process: (1) alkaline clean, (2) water rinse, (3) pickle, (4) water rinse, (5) neutralization, (6) zincate bath, (7) water rinse, (8) nitric acid dip, (9) clear chromate, (10) water rinse, (11) color chromate, (12) water rinse.

Table I. Analytical Results of Samples at the Zincate Bath Shop

No.	Plating Process	pH	Total Cyanide (mg/L)
1	Alkaline cleaning	—	N.D.
2	Water rinse	12.1	N.D.
3	Pickle	0.2	N.D.
4	Water rinse	0.9	N.D.
5	Neutralization	13.2	N.D.
6	Zincate bath	13.0	2.25
7	Water rinse	12.4	1.02
8	Nitric acid dip	1.0	0.94
9	Clear chromate	1.8	0.89
10	Water rinse	1.9	0.64
11	Color chromate	1.5	0.03
12	Water rinse	3.3	0.10
Wastewater Treatment Process			
A	Reservoir tank 1	12.4	2.18
B	Reservoir tank 2	11.7	0.54
D	Sedimentation tank	11.1	0.86
G	Chromate reservoir tank	3.5	0.14
F	Final pH adjustment tank	7.6	0.07

N.D., not detected.

samples are presented in Table I.

Although total cyanide was detected in every process solution after the zincate bath, it was not detected before the zincate bath. Especially high concentrations of total cyanide were detected in the zincate bath, water rinse, nitric acid dip, and clear chromate.

In the wastewater treatment process, high concentrations of total cyanide were detected in the acid/alkali reservoir tanks (Nos. 1 and 2) and sedimentation tank. Low concentrations of total cyanide were detected in the chromating effluent tank and final pH adjustment tank.

Total Cyanide in Plating-Process Solutions

Total cyanide in the zincate bath, nitric acid dip, and effluents at the

zincate bath shops was determined using the ISO, SM, and JIS standardized reference methods. The plating conditions and analytical results are presented in Tables II and III.

Six zincate solutions consisting of three barrel baths and three rack baths, which were obtained from five different shops, were examined. The main components of the zincate bath were zinc oxide, sodium hydroxide, and brighteners, which were synthesized from imidazole and epichlorohydrin.¹⁰

Total cyanide (0.44–16.8 mg/L) was detected in all zincate bath solutions when tested by the three standardized reference methods. Especially high concentrations of total cyanide were detected in the barrel baths (B,E). Furthermore, free cyanide was detected in the same zincate bath solution when

tested by the JIS method. Low concentrations (0.26–0.60 mg/L) of total cyanide and nitrite ion (12.4–22.2 mg/L) were detected in the nitric acid dipping solutions. In the case of the JIS method, total cyanide concentration was decreased, after decomposition of nitrite ion, in nitric acid dipping solutions by the addition of ammonium amidosulfuric acid.⁹ In addition, total cyanide was detected in the effluents (D,E) and decreased by the decomposition of nitrite ion.

Cyanide Formation by Electrolysis of the Zincate Bath

Zinc plating on steel was performed using a model zincate bath solution (12 g/L ZnO, 110 g/L NaOH, 10 ml/L brightener A, 1 ml/L brightener B), and the total cyanide concentration was determined at regular intervals. Electrolysis conditions were as follows.

The anode was a zinc plate (2.64 dm²), the cathode was a steel plate (2.64 dm²), the electrolysis current was 4 A, the voltage was 2–4 V, the cathodic current density was 1.52 A/dm², and the volume of the plating solution was 8 L. The relationship between plating time and total cyanide concentration is shown in Table IV.

Total cyanide concentration in the zincate bath was increased when accompanied by the electrolysis. A total cyanide concentration of 1.45 mg/L was detected after 88 hr of electrolysis. The results indicate that the cyanide ion is formed by the decomposition of a nitrogen-containing organic compound such as an imidazole derivative during zinc plating. As newer zincate

Table II. Zinc Plating Bath Conditions

Conditions/Shops	A	A	B	C	D	E
Equipment						
Plating process	Manual	Manual	Automatic	Manual	Semiautomatic	Manual
Plating bath	Barrel	Rack	Barrel	Rack	Rack	Barrel
Tank volume (L)	1,500	6,000	18,000	3,000	3,500	4,000
Composition						
Zinc metal (g/L)	6–9	7–13	10	5.7	8	10
Sodium hydroxide (g/L)	85–110	90–120	100	90	100	110
Brightener	IM-EP	IM-EP	IM-EP	IM-EP	IM-EP	IM-EP
Electro Conditions						
Applied potential (V)	11	9	—	9	6	8
Applied current (A)	1,000	2,000	—	1,200	400	2,400
C.C.D. (A/dm ²)	0.5–1	2–3	—	—	2	—
Plating time (min)	30	25	50	15	20	30

IM-EP, Imidazole epichlorohydrin derivative.
C.C.D., Cathode current density.

Table III. Total Cyanide Concentration in the Zincate Baths, Nitric Acid Dips, and the Effluents

Samples	Total Cyanide (mg/L)			NO ₂ ⁻ (mg/L)
	JIS ^a	ISO ^b	SM ^a	
Zincate Bath:				
C-S (new)	0.00	0.00	0.00	—
A-B	0.44	0.48	0.37	—
A-S	0.90	1.01	0.96	—
B-B	7.60	8.84	5.60	—
C-S	1.94	2.34	1.83	—
D-S	1.39	2.10	1.76	—
E-B	16.80	16.00	19.70	—
Nitric Acid Dip:				
A-B	0.42 (0.08) ^c	0.38	0.44	18.2
A-S	0.26 (0.24) ^c	0.24	0.26	22.2
B-B	0.23 (0.19) ^c	0.19	0.20	21.2
C-S	—	—	—	—
D-S	0.36 (0.13) ^c	0.36	0.27	17.0
E-B	0.60 (0.27) ^c	0.56	0.47	12.4
Effluent:				
A	N.D. ^c	N.D.	N.D.	8.4
B	—	—	—	—
C	N.D. ^c	—	—	19.1
D	0.29 (0.12) ^c	0.33	0.37	6.2
E	0.51 (0.47) ^c	0.44	0.50	13.8

N.D., Not detected.

^a In 100 ml distillate.

^b In 25 ml distillate.

^c Determined after the decomposition of nitrite ion by ammonium amidosulfuric acid.

bath solution was not applied, brightening on the surface of zinc plating disappeared after 100 hr of electrolysis.

Formation Mechanism of Cyanide

The formation mechanism of the cyanide ion in zincate bath shops is proposed as follows:

1. In these cases, brighteners in the zincate bath consist of imidazole and epichlorohydrin derivatives,¹⁰ which decompose and form the cyanide during zinc plating (see Fig. 3).

Tatsumoto¹¹ also reported that the cyanide ion was formed by the reaction of sodium hypochlorite and imidazole or hydantoin compounds, which are contained in the hospital effluent.

2. Plated zinc on the surface is dipped into nitric acid before chromating, and then part of the nitric acid is reduced to the nitrite ion. The nitrite ion in the effluent reacts with an organic compound such as EDTA⁹ in

an acidic solution during distillation to form hydrogen cyanide. When the nitrite ion is decomposed by ammo-

Table IV. Relationship between Plating Time and Total Cyanide Concentration

Electrolysis Time (hr)	Total Cyanide (mg/L)	Cyanide Formation (μg/A-hr)
0.0	0.00	—
16.6	0.19	22.9
50.0	0.67 ^a	26.8
88.3	1.45 ^a	32.8
142.0	2.53 ^a	35.6

^a Brightening disappeared.

nium amidosulfuric acid,^{8,9} the amount of hydrogen cyanide formed will be decreased.

References

1. Nonomura, M., *Toxicological and Environmental Chemistry*, 17(1):47-57; 1988
2. Nonomura, M., F. Nakagawa, S. Mizusawa, T. Ohno, H. Kobayashi, and T.

Hobo, *International Journal of Environmental Analytical Chemistry*, 39:371-379; 1990

3. Nonomura, M., *Industrial Water (Japan)*, 410:28-36; 1992
4. Nonomura, M., H. Ogino, and T. Hobo, *Aluminium*, 65(6):628-629; 1989
5. Nonomura, M., *International Journal of Environmental Analytical Chemistry*, 35:253-261; 1989
6. Nonomura, M., M. Suzuki, T. Hobo, K. Dejima, and H. Hotta, *Toxicological and Environmental Chemistry*, 39:65-70; 1993
7. ISO 6703/1, Part 1, International Standardization Organization, pp. 1-11; 1984
8. *Standard Methods for the Examination of Water and Wastewater*, 17th ed., pp. 4-20-4-25; American Public Health Association, Washington; 1989
9. JIS K0102, "Testing Methods for Industrial Wastewater," Japanese Standard Association, Tokyo, pp. 130, 156; 1993
10. Ohshima, K., H. Takasaki, and A. Takahashi, Japanese Patent No. 54-41544; 1979
11. Tatsumoto, H. and T. Hattori, *Environmental Technology Letters*, 9:1431; 1988

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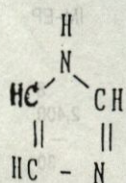
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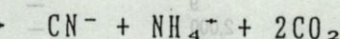


Figure 3. Decomposition reaction.