HEALTH HAZARD EVALUATION REPORT 71-1-4
HAZARD EVALUATION SERVICES BRANCH
DIVISION OF TECHNICAL SERVICES

Establishment: Midwest Steel Division
National Steel
Portage, Indiana

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Cincinnati, Ohio 45202

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SUMMARY DETERMINATION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees regarding exposures to electroplating solutions in the Electrolytic Tinning line at Midwest Steel Division of National Steel in Portage, Indiana.

Substances evaluated were fluorides, cyanides, hydrochloric acid and tin. The standard concentration levels for these substances are 2.5 milligrams per cubic meter (mg/M^3), 5.0 mg/M^3, 7.0 mg/M^3 and 2.0 mg/M^3 respectively.

An environmental survey was conducted on February 16-17, 1972 to determine exposures of twenty-five employees to fluorides, cyanides, hydrochloric acid and tin at the Electrolytic Tinning line. The fluoride concentration from air samples ranged from 0.17 to 0.59 milligrams per cubic meter (mg/M), tin concentration ranged from 0.01 to 0.20 mg/M^3, cyanide concentration ranged from 0.14 to 1.50 mg/M^3 and hydrogen chloride concentration ranged from 0.36 to 2.50 mg/M^3. The airborne concentrations of all these "individual" components in plating and rinsing solutions measured at the Tinning line were below the established standards (Federal Register, Part II, §1910.93, Table G-3) promulgated by the U.S. Department of Labor to prevent toxic effects characteristic of such substances. However, when exposure to two or more substances are present, as found in the Tinning line, the combined

effects rather than the individual exposure must be evaluated. The threshold limit value of the multiple exposures to fluorides, tin and cyanides was found to be exceeded in one location. The threshold limit value of mixture ranged from 0.1 to 1.3 where values greater than unity are in excess of the "standard of the mixture." Manifestation of adverse historical effects indicated from employee interviews were occasional minor eye and nose irritation.

Sound levels were also measured which approximated and exceeded in two locations the established standards for noise (Federal Register, Part II, §1910.95, Table G-16). Exposure to excessive noise levels can produce permanent hearing loss to man.

Based on multiple exposure concentrations calculated and a history of symptomatology obtained from employee interviews, it appears that a borderline health hazard currently exists from exposures to chemical substances investigated. Recommendations have been submitted to management to obviate observed and potential hazards and to provide a desirable working environment for all personnel.

Copies of this Summary Determination as well as the Full Report of the evaluation are available upon request from the Hazard Evaluation Services Branch, NIOSH, 550 Main Street, Cincinnati, Ohio 45202. Copies of both have been sent to:

a) Midwest Steel Division of National Steel
b) Authorized representative of employees
c) U.S. Department of Labor - Region V

For purposes of informing "affected employees," the employer will either (1) "post" the Summary Determination in a prominent place near where affected employees work for a period of 30 days or (a) provide a copy of the determination to each affected employee.

I. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees regarding exposures to sodium bifluoride, cyanide, tin and hydrochloric acid in the Electrolytic Tinning Line, TFG Department, Midwest Steel Division of National Steel, Portage, Indiana.

II. BACKGROUND HAZARD INFORMATION

A. Standards

The occupational health standards as promulgated by the U.S. Department of Labor (Federal Register, Part II, §1910.93, Table G-3) applicable to substances of this evaluation are as follows:

Fluoride (as F)	2.5 mg/M^3*
Tin (inorganic compound)	2.0 mg/M^3
Cyanide (as CN) - Skin	5.0 mg/M^3
Hydrogen Chloride	7.0 mg/M^3

B. Toxic Effects

Exposures to fluoride (as F), cyanide (as CN), tin, hydrochloric acid and cleaning solutions may manifest certain symptoms. Some of the physiological effects upon exposure to these agents are described below.

Fluoride toxic effects have been placed in three groups: (a) acute systemic intoxication (usually by ingestion), (b) local corrosion of the mucous membranes and skin and (c) chronic bone changes. Fumes in a magnesium foundry, containing fluorides in concentration above 10 mg/M^3 (milligram per cubic meter) were irritating and caused nosebleeds. Complaints of eye and respiratory passage irritation and nausea related to concentrations of 5 mg/M^3 have been reported.

*mg/M^3 - Milligram of contaminant per cubic meter of air

Cyanides are widely used in electroplating processes. The established standard of 5 mg/M^3 (milligram per cubic meter) for cyanides is based on the ability of its causing skin irritation and epistaxis (nosebleed) and nasal ulceration. The air concentration of cyanide from the cyanides producing this effect did not greatly exceed 5 ppm.

Tin salts, when they have gained access to the blood stream, are highly toxic producing paralysis and other neurologic damages. Exposure to dust and fumes of tin is known to cause stannosis, a benign pneumoconiosis. The fume is considered a more important source of stannosis than the dust. In the interest of preventing stannosis, a limit of 2 milligram per cubic meter is recommended.

Hydrogen chloride has been described as a strong irritant. Studies have indicated that exposures of men at 50-100 parts per million (ppm) for one hour was barely tolerable, 35 ppm caused irritation of the throat on short exposures and 10 ppm was the maximal concentration allowable for prolonged exposures. However, hydrogen chloride is immediately irritating when inhaled at concentrations of 5 ppm or more. Based on numerous reports, a TLV of 5 ppm is interpreted to be sufficiently low to prevent toxic injury, but on borderline of severe irritation.

Caustic cleaners, such a sodium hydroxide, are irritating to the upper respiratory system. Prolonged exposures to high concentrations may cause discomfort and even ulceration of nasal passages. Based on irritant effects of caustic mist, 2 milligram sodium hydroxide per cubic meter of air presented a concentration that was noticeable, but not excessively irritant.

III. HEALTH HAZARD EVALUATION

A. Initial Visit - Observational Survey

An initial hazard evaluation survey of the Tinning plating facilities, Midwest Steel Corporation was made on September 15, 1971, by NIOSH representatives Messrs. Jerome P. Flesch, Henry Ramos and Raymond L. Ruhe. The function of the National Institute for Occupational Safety and Health Act of 1970 and the purpose of the visit was explained to Mr. Collins, General Supervisor, Safety; Training and Community Relations. The National Surveillance Network questionnaire, Part I, was completed with his assistance. The Tin Plating process operates on a three-shift basis, employing a total of 34 operators.

Mr. Collins escorted us to the Tinning Plating process and introduced us to Mr. Bud Miller, Tin Plating foreman. Mr. Miller briefly explained and described the three levels in the Tin Plating facilities. The first level has 18 plating cells, second level 14 plating cells and the third level has a hydrochloric acid rinse vat. Each plating cell is approximately 10 feet long and 6 feet wide and contains about 2700 gallons of plating solution. The chemicals in the plating cells are identified as follows:

Stannous Chloride (62% Tin)	2.07 oz/gal
Sodium Bifluoride	3.95 oz/gal
Chloride	2.63 oz/gal
Sodium Ferrocyanide	0.087 oz/gal
duPont Agent No. 20	12 lbs/shift

The temperature range of the cells is maintained at 140-145°F and the amperage and voltage range is 3700-9000 ampere and 12-20 volts respectively. The amperage and voltage are adjusted to provide the desired coat thickness. Exhaust canopies over each cell connected to a master exhaust system. The conventional speed of the coiled metal passing through the cell is 1800 feet per minute; on "skinning tinning" the speed of the steel is reduced to 1600 feet per minute. Consumed tin electrodes are manually replaced. The rolls at the end of each cell are periodically cleaned or removed as needed. A hydrochloric acid vat which rinses the tin plated steel is situated on the third level.

Private interviews were conducted with a small number of employees. Manifestations of toxic effects indicated during these employee interviews were occasional coughing, burning of the eyes sensation, and acid burns on the job.

It was noted that approximately 25 feet from the Tin plating facilities, chrome plating facilities are being installed. Chemical emissions from the chrome facility presents a potential health hazard. Effective ventilation controls should be included in proposed chrome plating facility to preclude workroom air contamination.

Some areas of high noise were observed at various locations along the operating line.

B. Environmental Survey

On February 16-17, 1972 a follow up health hazard survey was conducted by Messrs. Ramos and Ruhe to determine exposures to fluorides, tin, cyanide and hydrochloric acid at the tin plating line. Cleaning

cells containing caustic and soda ash solutions are enclosed and provided with mechanical exhaust ventilation, consequently air samples were not collected. The average sampling time was approximately 6 hours. Both light and heavy tin coating were accomplished during the sampling period. The amperage and voltage of the cell was adjusted depending on the quality of coating desired. Messrs. Jack Wentz, General Supervisory Safety, John Paris, Safety Inspector and Robert Pastor, Union Chairman, Joint Management and Union Safety Committee, accompanied us during the evaluation.

Fluoride samples were collected in two midget impingers in series each containing 10 milliliters of 0.1N sodium hydroxide. Fluoride particulates were collected on Millipore Type AA 37 mm diameter, 0.8 micron pore size filters held in plastic field monitors. Stannous chloride samples were collected in two midget impingers in series each containing 10 milliliters of water. Sodium ferrocyanide air samples were collected in midget impinger containing 10 milliliters of 0.1N sodium hydroxide. The hydrochloric samples were collected in a midget impinger containing 10 milliliters of 0.5M sodium acetate. Each sampling device was equipped with a trap to prevent accumulation of medium in the pump. The air sampling rate maintained by use of MSA Model G portable pumps, ranged from 1.0 to 1.7 liters per minute. Additionally, some ventilation measurements were obtained on exhaust canopies over plating cells along with sound level measurements in areas of high noise along the line.

Results:

The air samples were analyzed by the Division of Laboratories and Criteria Development, NIOSH, Cincinnati, Ohio. Results of analysis mg/M^3 (milligram per cubic meter of air) are enclosed in Table 1. It should be noted that none of the measured concentrations of the air samples collected exceeded any of the individual established standards for substances evaluated.

However, when two or more hazardous substances are present, their combined effects, rather than that of either individually, must be considered. In the absence of information to the contrary, the effects of the different hazards must be considered as additive. That is, if the sum of the following fractions

$$\frac{C}{T} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \text{----} \frac{C_4}{T_n}$$

exceeds unity, then the threshold limit value of the mixture should be considered as being exceeded. C, C_2, C_3 are the observed concentrations of fluorides, tin and cyanides respectively and likewise T_1, T_2, T_3 correspond to the respective threshold limit value. Table II shows the summary results of multiple exposures on Tinning Line to fluorides, tin and cyanides.

The Alnor Velometer Jr. was used to spot check ventilation velocities on the plating cell exhaust canopies. Results are shown in Table III. Measured ventilation velocities were generally good, however, the relatively remote location of the canopy from the solution surface (18-24 inches above) precludes effective removal of airborne mists. Center canopy hood face velocities were not measured because accessibility to the center face of the canopy was very difficult. The velocities measured were taken at the leading edge of canopy hood.

The accumulation of crystallized chemicals on supporting beams and exhaust ducts indicates that significant quantities of plating chemicals are released into the workroom air and escape collection. On some cells the exhaust ventilation duct did not have a tight fit with the canopy hood. This will reduce the efficiency of the exhaust system.

Batch mixing conditions are poor. There are no controls which will prevent power chemicals from dispersing into the workroom air. Work is conducted in totally unsuitable location.

Although it has been established that "substances" as defined in Section 20(a)(6) of the Act does not include physical agents, for completeness of our overall responsibilities for acknowledging any occupational hazards we encountered during the evaluation at the work site, we report the following exposures to noise. Standards published in the Federal Register, Part II, §1910.95, Table G-16, are shown in Table IV. These standards are based on single reading of sound pressure level on the A-weighting network, slow response. Sound pressure level measurements were obtained using a General Radio, Sound Level Meter Type 1565-B. Results are shown in Table V indicating measured environmental sound levels and maximum allowable exposure per day without any hearing protection.

IV. CONCLUSION AND RECOMMENDATIONS

Based on multiple exposure concentrations calculated and a history of past symptomatology obtained from employee interviews, it appears that a borderline health hazard currently exists from exposures to chemical substances investigated. Recommendations are submitted to management to obviate observed and potential hazards and to provide a desirable working environment for all personnel.

1. The corporate industrial hygiene department personnel should solicit services of a private engineering firm to determine specific needs and institute controls for an effective exhaust ventilation system over the tin plating cells and proposed chrome plating vats. The present ventilation capacity appears satisfactory but is ineffective because of poor location.

2. A continuing effort should be made to maintain a clean plant. The accumulation of crystallized material on the ducts, hoods and area near the cells should be removed. Good housekeeping practices should be implemented.

3. A more suitable location for the mixing process under controlled exhaust ventilation should be instituted to prevent chemical dust infiltration into the environment. Bureau of Mines approved inorganic protective respirators should be made available to employees preparing chemical solutions in the batch mixing process.

4. Eliminate noise at its source by instituting feasible engineering controls. Employees working in high noise areas should be given periodic audiometric examination and be provided with protective hearing devices until noise levels are reduced to standard levels.

TABLE I

SUMMARY RESULTS OF ENVIRONMENTAL AIR SAMPLES

Sample	Substance	Location (Cell No.)		Concentration - mg/M^3
A	Fluoride (Gas)	Aisle Side	4	0.59
B	"	Aisle Side	12	0.21
C	"	Aisle Side	35	0.25
D	"	Aisle Side	29	0.23
E	"	Wall Side	5	0.26
F	"	Wall Side	15	0.58
G	"	Wall Side	35	0.17
H	"	Wall Side	29	0.20
A	Tin	Aisle Side	6	1.60
B	"	Aisle Side	15	0.10
C	"	Aisle Side	33	0.10
D	"	Aisle Side	26	0.10
E	"	Wall Side	8	0.10
F	"	Wall Side	16	0.10
G	"	Wall Side	33	< 0.01
H	"	Wall Side	25	0.20
A	Cyanide	Aisle Side	9	1.5
B	"	Aisle Side	17	0.62
C	"	Aisle Side	31	0.60
D	"	Aisle Side	24	0.56
E	"	Side Wall	12	0.88
F	"	Side Wall	18	0.14
G	"	Side Wall	31	0.21
H	"	Side Wall	24	0.33
A	Hydrogen Chloride	3rd Level		2.50
B	"	3rd Level		1.70
C	"	3rd Level		0.36
D	"	3rd Level		0.52

TABLE I - Cont'd

Sample	Substance	Location (Cell No.)		Concentration - mg/M*
1A	Particulate (Fluoride)	Aisle Side	31	0.87
2A		Aisle Side	24	1.30
4A	"	Aisle Side		0.20
5A	"	Work Table		0.36
1B	"	Wall Side	35	1.80
2B	"	Wall Side	29	0.74
3B	"	Work Table		0.38
4B	"	Wall Side	5	1.00
5B	"	Wall Side	15	1.20

* Time-weighted average concentration of substances in milligram of contaminant per cubic meter of air.

TABLE II

SUMMARY RESULTS OF MULTIPLE EXPOSURES ON
TINNING LINE TO FLUORIDES, TIN AND CYANIDES

LOCATION			THRESHOLD LIMIT VALUE OF MIXTURE
Aisle Side			
Samples No.	A	Cell Nos. 4, 6 & 9	1.3
	B	12,15 & 17	0.3
	C	29,26 & 31	0.2
	D	35,35 & 24	0.3
Wall Side			
Samples No.	E	Cell Nos. 5, 8 * 12	0.3
	F	15,16 & 18	0.3
	G	25,33 & 24	0.2
	H	35,25 & 31	0.1

TABLE III

SUMMARY VENTILATION MEASUREMENT FOR CANOPY HOODS AT TIN PLATING CELLS

First Level Aisle Side Beam No.	Center Face Velocity* (FPM) at Leading Edge of Canopy Hood 18-24" Above Plating Solution	Face Velocity* at Accessible End of Ca 18-24" Above Plating So
C-4	200	200
R-3	150	150
R-4	300	180
R-5	200	160
R-6	300	200
C-10	400	175
R-8	400	175
R-9	410	175
R-10	400	200
R-11	600	175
R-12	490	300
R-13	300	200
R-14	400	200
R-15	300	175
R-16	250	200
R-17	200	125
R-18	150	75
R-19	200	200

* Velocity measured in linear feet per minute (FPM).

TABLE III- Cont'd

SUMMARY VENTILATION MEASUREMENT FOR CANOPY HOODS AT TIN PLATING CELLS

Second Level Wall Side Beam No.	Center Face Velocity* (FPM) at Leading Edge of Canopy Hood 18-24" Above Plating Solution	Face Velocity* at Accessible End of Ca 18-24" Above Plating So
C-35	0-50	0-50
C-34	200	150
C-32	220	175
C-32	400	200
C-31	400	200
C-30	300	175
C-29	300	150
C-28	400	300
C-27	300	200
C-26	200	200
C-24	200	150
C-23	200	170
C-22	125	75
C-21	125	0-25

TABLE IV

PERMISSIBLE NOISE EXPOSURES*

Duration Per Day, Hours	Sound Level dBA Slow Response
8	90
6	92
4	95
3	97
2	100
1-1/2	102
1	105
1/2	110
1/4 or Less	115 Ceiling Value

* When the daily noise exposure is composed of two or more periods of noise exposure of different levels, their combined effect should be considered, rather than the individual effect of each. If the sum of the following fractions: C1/T1+C2/T2+Cn/Tn exceeds unity, then the mixed exposure should be considered to exceed the limit value. Cn indicates the total time of exposure at a specified noise level, and Tn indicates the total time of exposure permitted at that level.

Exposure to impulsive or impact noise should not exceed 140 dB peak sound pressure level.

TABLE V

SUMMARY NOISE MEASUREMENTS

Cell No.	Location	Measured Sound Level, dBA	Maximum Daily Exposure, Hours
First Level:			
C-13	Aisle Side	87	>8
C-16	Aisle Side	87	>8
C-19	Aisle Side	89	>8
C-21	Aisle Side	89	8
	Work Order Desk	85	>8
Second Level:			
23	Aisle Side	90	8
25	Aisle Side	95	4
27	Aisle Side	89	8
30	Aisle Side	86	>8
33	Aisle Side	89	8
35	Aisle Side	82	>8
Third Level:			
	Aisle Side Near Hydrochloric Acid Vat	94	4