

METAL FINISHING

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COVER

Palladium coated parts illustrate this issue's electroless plating theme. Parts courtesy of Callery Chemical Co. Photography by Don Vellekamp, Creative Marketing, Fairfield, NJ.

EDITORIAL

What's in a Name?

Whether you call it chemical plating, autocatalytic deposition, or simply electroless plating, the fact remains that this process has become important for metal finishers and their customers.

There once was a time when such procedures were seldom used and then only in odd circumstances. Remember the bronzed baby shoes?

Nowadays things have changed. The technique ensures uniform coverage even with blind holes and deep recesses. The many diverse, and important, applications are in accord with the nature of the metal deposited.

Electroless copper is used for its conductivity in the through-hole plating of printed circuit boards. Electroless nickel alloys are used in turn for their corrosion and wear resistance in the chemical industry and in oil field equipment or for good wire bonding and solderability in the electronics field.

Electroless gold and palladium are ideal for connector applications. Electroless cobalt is the material of choice in magnetic memory discs which include an underlayer of nonmagnetic electroless nickel.

The plating of plastics has been a big booster for electroless coating. Decorative finishes for the automotive industry and plumbing specialties are standards. Electroless copper and nickel coatings provide the best in attenuation for EMI/RFI shielding of electronic enclosures.

The importance of this subject leads to the articles incorporated in this special issue. We hope they will inform you as to the many aspects of this once neglected process, no matter what you may call it.

Michael Murphy

EDITOR

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METAL FINISHING

Environmental Study of a Plating Room

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DESCRIPTIVE ANALYSIS AND HAZARD EVALUATION

This paper reports on the reorganizing of a plating room (including surface preparation, conversion coating and electroplating) in an electromechanical factory in order to improve the work environment. The workforce concerned was increased from 16 (before the operation) to 20. The amount of material plated (steel and copper) was approximately 12,000 kg per eight-hour day.

To set the priorities for the reorganization, a descriptive analysis of the process cycles and plants in the plating room was made.

In identifying the raw materials used in the different processes and the contaminants that may be released, a toxicity index referred to the threshold limit values in workroom air (ACGIH TLV-TWA, 1984). The evaluation of the different toxicity classes (A>B>C>D) was made following these criteria:^{1,2}

1. Index A refers to substances with $TLV \leq 10$ ppm in the case of gas and vapors or $TLV \leq 0.1$ mg/m³ in the case of mists.

2. Index B refers to substances respectively with $10 < TLV \leq 100$ ppm or $0.1 < TLV \leq 1$ mg/m³.

3. Index C refers to substances respectively with $100 < TLV \leq 500$ ppm or $1 < TLV \leq 10$ mg/m³.

4. Index D refers to substances respectively with $TLV > 500$ ppm or $TLV > 10$ mg/m³.

In identifying the process parameters such as temperature, concentration, agitation, substance volatility, gassing, etc., an emission index was introduced.^{1,2} The different processes were classified into four categories (1>2>3>4) making a relative scale of the contaminant evolution:

1. Index 1 refers to the emissions from the organic solvent cleaner at high temperature and the chromium plating bath at moderate temperature.

2. Index 2 refers to the emissions

from the pickling baths at moderate or low temperature, the phosphating and the anticorrosive treatment baths at high temperature, and the alkaline tin plating bath at high temperature.

3. Index 3 refers to the emissions from the electrolytic cleaning baths operated with no heating, the passivation bath and the zinc and copper plating baths.

4. Index 4 considers greatly diluted acid baths (neutralization, bright dip) and silver and cadmium plating baths at low temperature, from which the emissions are much more reduced.

The emission index is then corrected taking into account the effectiveness of the method used for the emission control, following these criteria:

1. No local ventilation: emission index unchanged.

2. Local ventilation by means of canopy hood: emission index + 1.

3. Local ventilation by means of lateral hood: emission index + 1.

4. Local ventilation by means of push/pull hood: emission index + 1.

5. Local ventilation by means of enclosing hood: emission index + 2.

6. Complete enclosure of process equipment: emission index + 3.

7. Isolation of process area: emission index + 3.

Combining the toxicity index to the emission index adjusted to the existing control methods, different hazard classes are determined as described in Table I.²

In Table II, the descriptive analysis result is reported, carrying out a preventive hazard evaluation related to the different process cycles. Considering the high level of hazard, a priority of operation has been given to the following cycles: solvent cleaning; acid pickling; chrome passivation; cadmium plating; and chromium plating.

REORGANIZING THE OPERATION

Very few modifications have

Table I. Hazard Class Assessment

Emission Index	Toxicity Index			
	A	B	C	D
1	I	II	III	V
2	I	II	III	V
3	II	III	IV	VI
4	III	IV	VI	VI

been effected in the production cycles where most of the work is operated, nevertheless they have been completely automated (except for the loading and unloading phases for which an automation study is to be completed). The main cycles are the following ones:

1. Phosphating and anticorrosive treatment on steel parts with an average of 300 kg per eight hr.

2. Alkaline cyanide zinc plating on steel parts in the average of 6000 kg per eight hr.

3. Acid tin plating (replacing the above alkaline one) on copper parts in the average of 1000 kg per eight hr.

4. Alkaline cyanide silver plating on copper and copper alloy parts in the average of 4500 kg per eight hr.

The plating room layout before and after the reorganizing operation is visualized in Figs. 1A and 1B. Before the reorganization, the main cycles were performed in a complicated and inefficient material flow inside the plating room; further, different processes interfering with those performed in the pretreatment area, have been moved.

In Table III the plants with the modifications that have been completed are listed. It can be observed that, in many cases, the reorganization is a result of the combination of different actions.

ACTIONS COMPLETED

PRODUCTION CYCLE:

1. Alkaline pickling is removed, avoiding the processing of greatly oxidized materials.

2. Descaling by phosphates and bisulfates for copper parts and by

Table II. Hazard Evaluation Related to the Different Processes

Process	Main Steps	Emission Control by Local Ventilation	Toxicity Index (Step)	Emission Index (Step)	Hazard Class (Process)
Solvent cleaning	Immersion cleaning in perchloroethylene (120°C)	Lateral hood	B	1+1	II
Alkaline pickling	Pickling in caustic soda solution (50°C)	Canopy hood	C	2+1	IV
Acid pickling	Pickling in hydrochloric and phosphoric acid solution	Lateral hood	A	2+1	II
	Pickling in sulfuric and nitric acid solution	Canopy hood	A	2+1	II
Phosphating	Phosphating in zinc phosphate bath (70°C)	Lateral hood	B	2+1	III
Anticorrosive treatment	Treatment in buffered stannic chloride solution (90°C)	" "	C	2+1	
Passivation	Passivation in chromic acid solution	No local ventilation	A	3	II
Zinc plating (rack and barrel)	Anodic cleaning in caustic soda and cyanide solution	Lateral hood	C	3+1	III
	Acid neutralization	" "	A	4+1	
	Plating in cyanide bath	" "	C	3+1	
	Bright dip in nitric acid solution	" "	A	4+1	
Silver plating (rack and barrel)	Cathodic cleaning in caustic soda and cyanide solution	No local ventilation	C	3	III
	Acid neutralization	" "	A	4	
	Alkaline copper plating in cyanide bath (50°C)	Lateral hood	B	3+1	
	Silver strike plating	" "	A	4+1	
	Silver plating in cyanide bath	" "	A	4+1	
Tin plating (rack)	Plating in sodium stannate bath (80°C)	Lateral hood	C	2+1	IV
Cadmium plating (rack)	Chrome passivation	No local ventilation	A	3	II
	Acid neutralization	" "	A	4	
	Electrolytic cleaning	Canopy hood	C	3+1	
	Plating in cyanide bath	" "	A	4+1	
Chromium plating	Hard chromium plating in chromic and sulfuric acid solution (50°C)	Enclosing hood	A	1+2	II

Notes: 1. The hazard class is indicated by referring to the most toxic contaminant released during the process.
2. Room temperature when not indicated.

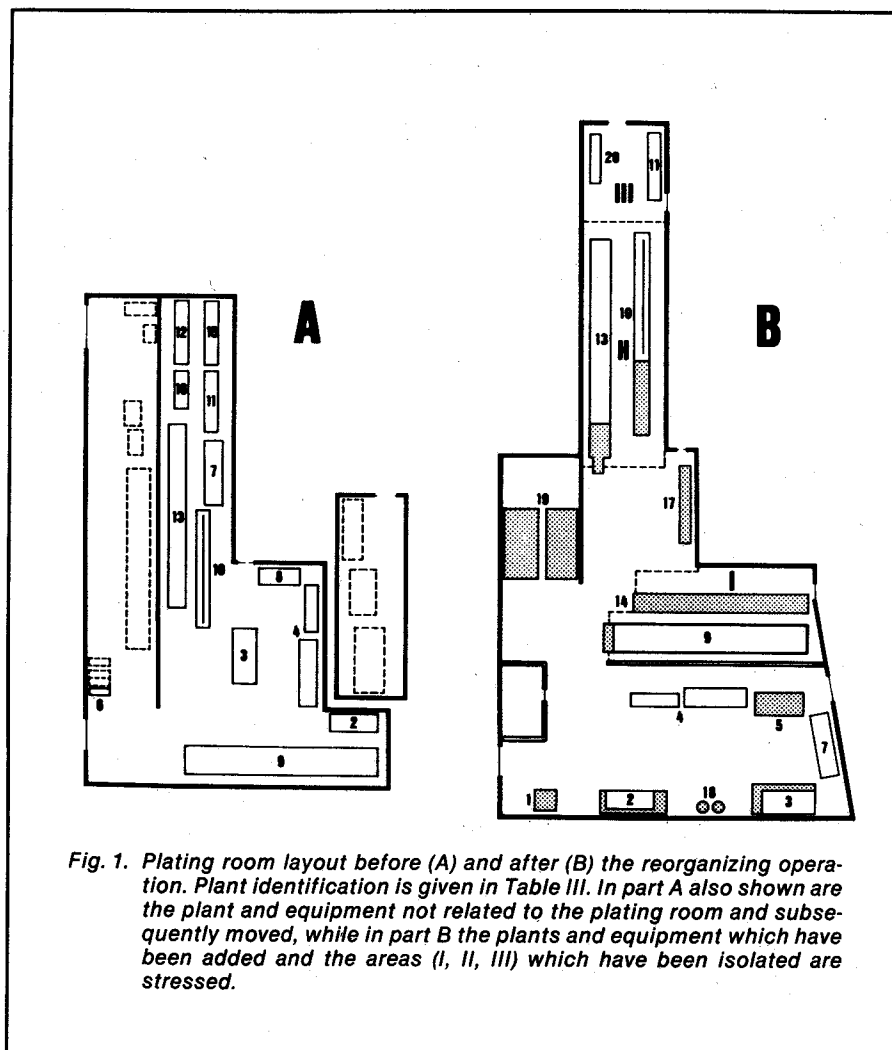


Fig. 1. Plating room layout before (A) and after (B) the reorganizing operation. Plant identification is given in Table III. In part A also shown are the plant and equipment not related to the plating room and subsequently moved, while in part B the plants and equipment which have been added and the areas (I, II, III) which have been isolated are stressed.

hydrochloric acid for steel parts, is added.

3. Phosphating and chrome passivation are included in the processing cycles.

4. Alkaline tin plating is replaced by acid tin plating.

5. Cadmium plating is replaced by zinc impact plating (this process is performed outside the plating room).

6. Chromium plating is removed.

LAYOUT:

1. The plating room floor area is enlarged from 900 to 1360 m².

2. The surface preparation area is separated from the electroplating area.

3. Substance storage (cyanides, hydrochloric acid, etc.) is moved outside the plating room.

4. Cyanide solution preparation is centralized.

5. Interferences between transit areas and working areas and between workers of different processing cycles are avoided (e.g. painting area is moved away).

PLANT AND EQUIPMENT:

1. New grit blasting unit (with rotary table).

2. New descaling unit.

3. A drying oven is included in the silver rack plating plant.

4. New plant for silver and tin barrel plating.

5. New oven to dry zinc rack plated parts.

6. New equipment for organic solvent recovery (by adsorption on activated carbon and desorption with steam).

WORK PRACTICES:

1. Dipping time is revised during the solvent cleaning treatment and blowing time is extended.

2. All manual dipping operations are avoided during acid pickling, phosphating and chrome passivation processes.

3. The tin plating cycle is automated.

4. Compressed air, used in the zinc rack plating cycle to dry parts, is removed.

EMISSION CONTROLS:

1. Complete enclosure of organic solvent cleaning units.

2. Local ventilation is placed over all the treatment and plating tanks.

3. Floating plastic balls are used in all the barrel plating tanks.

4. Isolation by glass walls of the

electroplating lines (the workers' exposure is limited to the maintenance and plant cleaning phases).

5. New equipment to supply makeup air to the enclosed spaces and the whole workroom. The makeup air supply to the zinc and silver/tin barrel plating area (I) is approximately 20,000 m³/hr, while the supply to the zinc and silver rack plating area (II) is approximately 26,000 m³/hr. The air changes in these enclosed spaces 20 times per hour. For area (III), containing the zinc rack plating plant, the air supply is approximately 4000 m³/hr, which means six air changes per hour. For the whole workroom, with the exception of the enclosed spaces, the air changes are approximately nine times per hour. The enclosed spaces are kept under a slight suction of a few millimeters water column, so as to prevent contaminants released by electroplating processes from leaking into the workroom air. (In the previous situation the general ventilation was inadequate and the local ventilation was applied only to a few tanks).

ENVIRONMENTAL MEASUREMENTS

Together with the descriptive analysis concerning the plant focusing on the less adequate situations, contaminant measurements with fixed samplings have been performed to better evaluate the acceptability of the work environment and find out the most critical places in view of the reorganizing operation.

Additional measurements have been performed after the plating room reorganization. All the results are reported in Table IV.

To assess the acceptability of the work environment the criteria based on the One-Sided Tolerance Limits (OTL),³ have been adopted assuming as a standard concentration (STD) for the contaminants the corresponding TLV-TWA (ACGIH, 1984). The test performed was for 95% confidence (1- α = 0.95) that less than 5% of all concentrations (P = 0.95) exceed STD.

The application of the OTL decision criteria, referring to the situation before the reorganization, is illustrated in Fig. 2A while 2B refers to

Table III. Plating Room Before and After the Reorganization: Plant Identification and Action Classification

	Plant Identification (Note 1)		Productive Cycle	Layout	Action Classification (Note 2)			
	Before Reorganization	After Reorganization			Plant and Equipment	Work Practice	Emission Control	
Surface preparation	Solvent cleaning	1 Grit blasting	+		+			
	Solvent cleaning	2 Solvent cleaning		x		x	x	
	Alkaline pickling	3 Solvent cleaning	*	x		x	x	
	Acid pickling	4 Acid pickling		x		x	x	
		5 Descaling		+		+	x	
Conversion coating	Phosphating	6 Anticorrosive treatment				x		
	Anticorrosive treatment	7 Anticorrosive treatment		x			x	
	Chrome passivation	8				x		
Electroplating	Zinc barrel plating	9 Zinc barrel plating					x	
	Zinc rack plating	10 Zinc rack plating		x		x	x	
	Silver barrel plating	11 Zinc rack plating	x	x		x	x	
	Tin rack plating	12	*					
	Silver rack plating	13 Silver rack plating				x		x
		14 Silver/tin barrel plating		+		+		x
		15	*					
Cadmium plating	16	*						
Post-treatments	Chromium plating	17 Drying oven for zinc rack plated parts			+			
Auxiliaries		18 Solvent recovery			+		x	
		19 Makeup air treatment			+		x	
		20 Cyanide solution preparation		x				x

Notes: 1. See Figures 1A and B.
2. x means modification, + addition and * removal.

Table IV. Contaminant Sampling Results Before and After the Plating Room Reorganization

Plant Identification	Contaminant	STD (mg/m ³)	Sampling Number	GM (mg/m ³)	GSD	OTL Test Statistic
<i>Before Reorganization</i>						
2 Solvent cleaning	Perchloroethylene	335	5	101.1	3.31	1.00
3 Solvent cleaning	Perchloroethylene	335	5	182.6	2.18	0.78
7 Anticorrosive treatment	Zinc	5	4	0.039	2.88	4.59
	Tin	2	3	0.052	1.70	6.88
9 Zinc barrel plating	Zinc	5	4	0.388	2.28	3.10
10 Zinc rack plating	Zinc	5	3	0.693	1.32	7.02
	Cyanide (as CN)	5	5	0.12	3.00	3.39
	Silver	0.01	4	0.006	2.36	0.59
11 Silver barrel plating	Cyanide (as CN)	5	4	0.43	2.38	2.83
	Tin	2	3	0.117	1.69	5.41
15 Cadmium plating	Cadmium	0.05	3	0.028	4.59	0.38
<i>After Reorganization</i>						
2 Solvent cleaning	Perchloroethylene	335	13	14.6	1.91	4.84
3 Solvent cleaning	Perchloroethylene	335	10	18.8	2.09	3.91
5 Descaling	Hydrochloric acid	7	4	1.13	1.62	3.78
7 Anticorrosive treatment	Zinc	5	12	0.021	1.74	9.88
	Tin	2	12	0.065	1.80	5.83
<i>Isolated Area, I</i>						
9 Zinc barrel plating	Zinc	5	8	0.003	1.40	22.05
14 Silver/tin barrel plating	Tin	2	8	0.016	1.65	9.64
	Silver	0.01	8	0.002	1.77	2.82
	Copper	1	8	0.003	1.32	20.92
<i>Isolated Area, II</i>						
10 Zinc rack plating	Zinc	5	8	0.009	1.56	14.21
13 Silver rack plating	Silver	0.01	8	0.003	1.56	2.71
	Copper	1	8	0.009	2.88	4.45
<i>Isolated Area, III</i>						
11 Zinc rack plating	Zinc	5	4	0.010	1.69	11.84
Center Room, CR outside the isolated areas	Zinc	5	8	0.007	1.45	17.69
	Silver	0.01	9	0.003	1.40	3.58
	Copper	1	9	0.007	2.39	5.69

Notes: 1. For plant identification see Figs 1A and B. STD = standard concentration (ACGIH TLV-TWA, 1984), GM = geometric mean concentration (lognormal distribution), GSD = geometric standard deviation of concentrations (lognormal distribution), OTL test statistic = $(\log \text{STD} - \log \text{GM}) / \log \text{GSD}$, OTL = One-sided tolerance limits.

2. Material and methods: Fixed samplings with samplers placed on the tank edge or in the positions occupied by the workers during the regular working of plants, sets of simultaneous samplings (spatial distribution) or sets of sequence samplings (temporal distribution), sampling durations 2 to 4 hr. Metals: collection on 0.8 μm microporous filters, dissolution in concentrated nitric acid, determination by plasma spectrometer. Cyanide and hydrochloric acid: impinger collection, determination by ion selective electrode. Organic solvent: adsorption on activated carbon, desorption with carbon disulfide, determination by gas chromatograph.

the new situation. The points representative of the situation before the reorganizing operation indicate a great extent of indecision concerning the acceptability/unacceptability of the work environment. After the reorganization, indications for a complete acceptability are given, with a few exceptions due to the insufficient number of measurements performed.

It is noted from Table IV that the dispersion index (GSD) values referring to the measurements performed after the reorganization are lower, indicating a better contaminant control for the more adequate ventilation systems adopted. In addition, the results obtained by environmental monitoring reflect the ef-

fectiveness of the various methods used for the control of the emissions generated by the different processes.

Thus, the reinforcement of local ventilation on the anticorrosive treatment tank, as shown by the increase in the test statistic, yields an improvement which is lower compared to those obtained with the complete enclosure of the solvent cleaning units and the isolation of the electroplating lines.

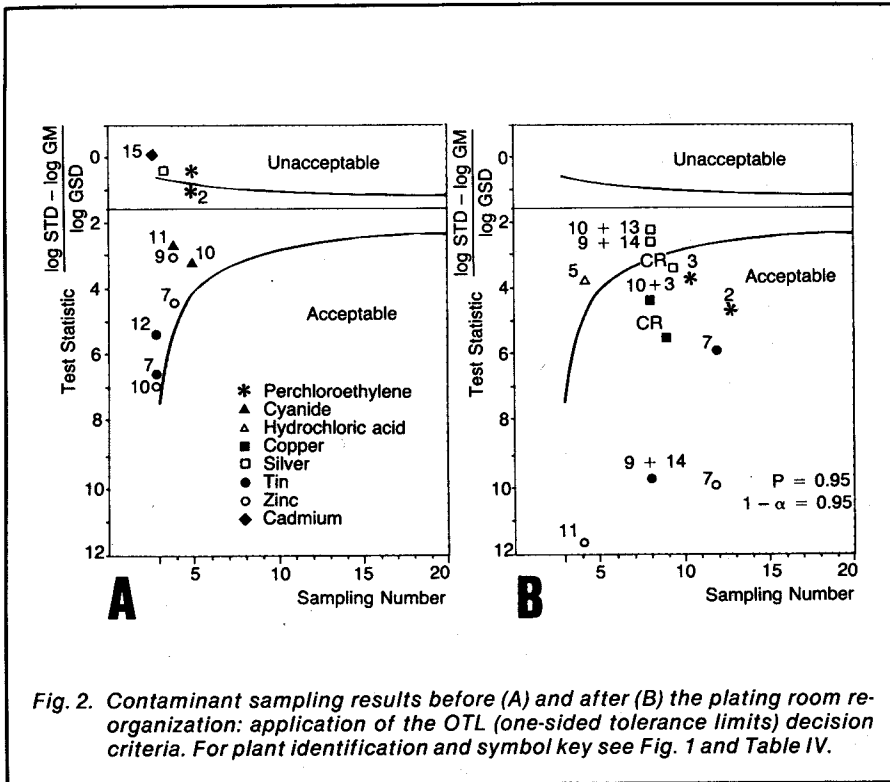
CONCLUSION

A preventive hazard assessment of process and plant together with environmental monitoring have been accomplished to find out the most critical places in the plating

room and evaluate the degree of the problem. This combination has given a positive indication to the reorganizing operation.

Even in a productive field like the plating industry, in which the workers' health hazards caused by occasional exposures to or contacts with toxic substances may be prevalent, the measurement of contaminant concentration in workroom air can be a good indicator of the situation.

The isolation by glass walls of the electroplating lines, the complete enclosure of the organic solvent cleaning units, the improvement of all local ventilation, determined by a more adequate suction, and the new equipment to supply makeup



air to isolated spaces and the whole plating room, make the work environment largely acceptable. The reorganizing operation presents, in this respect, favorable results.

Environmental monitoring has been very useful in the setting up of a checking program, to be repeated every 8 to 12 months. It requires a reasonable number of measurements of substances considered contamination indicators. This will apply to perchloroethylene and hydrochloric acid in the surface preparation area, and silver in the electroplating area.

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