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**Project Summary** 

## Alkaline Noncyanide Zinc Plating and Reuse of Recovered Chemicals

Jacqueline M. Peden

A metal finishing process can create environmental problems because it uses chemicals that are not only toxic but also resistant to degradation or decomposition. A study was undertaken at a zinc electroplating operation to achieve zero discharge of wastewater and total recycle of recovered precipitates. The first step in this project was to change an existing zinc cyanide (CN) plating line to one that used an alkaline noncyanide (ANC) zinc bath. The project then investigated a closed-loop system to treat plating rinsewater from the ANC zinc plating line so the plating chemicals were recovered and the water purified. The goal was to return both the recovered zinc hydroxide and the clean water to the plating line for continued use. The system that was designed and installed, at P&H Plating Co., a Chicago area operation used precipitation by pH adjustment to remove the zinc from the rinsewater. The precipitated zinc hydroxide was collected on filters, dewatered using a filter press, and stored for reuse in the plating line as needed. Once filtered, the water was recirculated to the rinsing portion of the plating line. The recovery/recycle system successfully purified the rinsewater and facilitated the recycling of the cleaned water and the precipitated zinc hydroxide. Eliminating cyanide from the plating process meant the line workers were dealing with a less toxic plating bath, made compliance with regulations easier, and re-

duced treatment and disposal costs for the company. The recycling of the recovered water and the zinc hydroxide further reduced the costs for treatment and disposal. The replacement of this single CN line with an ANC line resulted in an annual savings to P&H Plating of \$14,000 from the elimination of the need to pretreat the plating line rinsewater to oxidize cyanide. The addition of the recovery/recycle system increased the company's savings to \$62,000/yr. The reuse of 30% of the recovered zinc hydroxide and 70% of the treated rinsewater reduced annual water usage and wastewater discharge by 841,911 gal and reduced the amount of sludge disposed annually by 14 yd<sup>3</sup>. The payback period for the recovery/ recycle system is slightly less than 18 mo. Installation and use of this system for other ANC plating operations would result in reductions in wastes and increased economic benefits similar to those experienced by P&H Plating Co.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the WRITE program demonstration that is fully documented in a separate report of the same title (see Project Report ordering information at back).

#### Introduction

This cooperative effort between the U.S. Environmental Protection Agency (EPA) and the Illinois Hazardous Waste Research and Information Center (HWRIC) was undertaken to evaluate the feasibility of using an innovative, closed-loop rinsewater treatment system to precipitate plating chemicals for recovery and reuse and to produce purified water for recirculation to the rinsing tanks and sprayers. The goal of this study was to achieve zero discharge of the wastewater and total recycle of the recovered precipitate thereby reducing the amount and toxicity of the waste from an electroplating shop's zinc plating operation. The CN plating line was converted to one that used an ANC plating bath. A recovery/recycle (R/R) unit was then designed, installed, and tested to determine how completely the goals of the project were being met. The effectiveness of the R/R system in reducing the process wastes was evaluated by: quantifying the effectiveness of the removal of the zinc through precipitation by pH adjustment (the basis of the recovery system); determining the quality of the precipitate and the treated water that were recovered; comparing the plating quality of the CN-based operation to that of the ANC-based processes and analyzing the costs associated with the change in the process and the installation of the R/R system. The R/R unit was designed, installed, and tested by engineers from the Center for Neighborhood Technology (CNT). Their initial analysis that the system would be effective in reducing wastes and facilitating recycling of the bath components was confirmed by HWRIC engineers who again tested the system after more than 1 yr of operation. A slightly modified unit that accommodates two plating lines, rather than one, is still in operation at P&H Plating Co. after more than 3 yr.

#### **Industry Partner**

P&H Plating Co. is one of 174 plating operations in Cook County, Illinois. It is a large job shop that operates 16 hr/day, 6 days/wk. It uses barrels, hoists, and racks to move parts through the plating process. Although this project concentrated on zinc plating, the shop is capable of and does plate nickel, brass, copper, and cadmium on a variety of surfaces. The facility contains a waste treatment area that receives effluent at an average rate of 150 gal/min. For this project, the company made two changes to one of its barrel plating lines. It replaced a CN plating line with one that used an ANC bath and installed the CNT-designed R/R system. An evaluation of the effectiveness of these changes continued over 2 yr.

#### **Problem Statement**

Achieving waste reduction in the electroplating industry is important because the wastes can create many environmental problems. The chemicals used are not only toxic but also resistant to degradation or decomposition. Many opportunities are open to electroplaters to reduce their wastes. Simple housekeeping techniques such as slowing down the movement of parts through the operation to increase drain time can significantly reduce the amount of plating bath chemicals carried over into the wastewater. Other options include recovering bath chemicals, cleaning and recycling rinsewater, using less toxic chemicals when possible, and using technologies such as ion exchange to clean and maintain plating baths. Adopting these types of process modifications are generally not only environmentally advantageous but frequently result in economic benefits.

Federal and state regulations set limits on the amounts of toxic plating line constituents that can be discharged. The costs to comply with these regulations can be considerable. Cyanide is a particularly difficult contaminant to treat: it readily combines with metals, particularly iron, to form stable complexes that may not be destroyed by standard treatment methods. It poses substantial health and environmental risks if not handled correctly or treated completely. Enforcement efforts on both the state and federal levels are well coordinated, and prosecution of violators has increased. Electroplaters must develop an integrated approach to waste management that meets compliance standards and includes waste reduction as a vital component.

### The CNT Recovery/Recycle (R/R) System

The relatively simple principles involved in the design of the CNT R/R system are similar to those for a standard wastewater flocculation treatment to remove metals before disposal of water and sludge wastes. Ideally, 100% of the zinc in the CNT R/R system's rinsewater would be recovered and returned to the plating bath. Additionally, all rinsewater would be recycled. The projected result would be substantial savings for the company in plating chemicals and water from this rinsewater purification that both recovers and reuses as well as treats.

In the plating process at P&H, there is the usual parts pretreatment or cleaning, followed by the plating process, a spray rinse, and finally, submersion into two counterflow rinse tanks. Although cleaning requirements for ANC plating are generally more stringent than those for CN plating, no change was required to the pretreatment portion of the line at P&H. The company had already installed a very stringent cleaning component to their plating lines to ensure good parts cleaning and, presumably, better plate quality. The CNT R/R system was plumbed from the spray rinse tank into which the counter flow tanks ultimately overflowed. The rinsewater flows into a tank where the pH is measured and automatically adjusted to a pH between 10 and 10.5.

This pH monitoring and control tank is a continuous flow stirred reactor (CFSR). It is designed to stimulate precipitation by sparging with compressed air entering from the bottom of the tank. The flow rate through the CFSR is set at 10 gal/min. The precipitate/water slurry next flows into a flat-bottomed clarifying tank. To facilitate the settling process, the tank is baffled. A recirculating pump is used to pull water from the clarifying tank through the dual filtering system to remove suspended hydroxide. The filtered water then either flows to a storage tank for reuse or to the waste treatment area for disposal. The precipitate that has settled in the clarifying tank is removed and combined with that collected on the filters. This composite hydroxide is placed in a filter press to remove as much water as possible. The water that is removed is returned to the precipitation reactor and the dewatered hydroxide is analyzed and stored for future use or disposed if not needed. Figure 1 shows the system components and the path of the water and the solids as they flow through the system.

#### **R/R System Performance**

Although the system had problems, it proved to be a highly efficient and economically advantageous addition to the plating operation. The quality of the zinc hydroxide precipitate and the purified water were sufficient for recycling. Careful

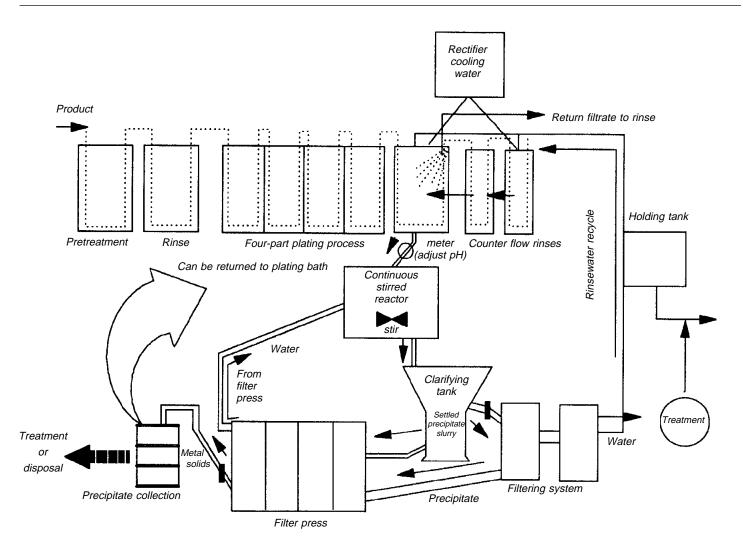


Figure 1. P&H Plating alkaline noncyanide plating line with CNT designed recovery/recycle system.

and regular analysis of the essential bath chemicals is recommended to ensure contaminants are not introduced through these recycling efforts.

The CNT R/R system has been in continuous operation for over 3 yr. Maintenance consists of proper care of the mechanical parts and periodic replacement and cleaning of the filters. Zinc hydroxide is removed from the rinsewater with an efficiency averaging 84%. The amount of precipitate recycled to the bath depends largely on the number of jobs requiring use of that line. The company estimates that it recycles 30% of the zinc hydroxide it recovers. The quality of the purified water is generally acceptable for recycling or for discharge. Approximately 70% is used in the rinsing operation or to replenish the plating bath. The system works well providing both environmental and economic benefits to P&H.

#### Plating Quality Comparison

Although the reasons for plating are sometimes purely ornamental, more frequently the plate is for protection. Finishes may be bright or dull, and it may not always be possible to achieve the desired luster with the ANC system. Advances in the last decade have, however, provided less toxic bath alternatives that produce parts more like the bright, shiny objects that result from a CN-based operation. Ultimately, whether the plate is satisfactory or not is up to the customer, but two commonly used standard tests can be performed to evaluate quality—thickness and corrosion resistance. When parts plated on both the CN and ANC lines were compared for these standards, both processes produced parts with the desired thickness and acceptable corrosion protection.

#### **Toxicity Comparison**

Had there been no economic benefit from the change to ANC plating, the reduction in health and environmental risk resulting from the elimination of cyanide from the process would have been sufficient to warrant its adoption. CN plating requires extensive treatment before disposal and uses chemicals hazardous to human health. Chemical substitution to achieve source reduction, as was done for this project, not only reduced process costs but also the company's liability because of the reduced toxicity of the chemicals being handled and disposed.

The exposure of shop workers to toxic chemicals presents the most serious health and safety problems for the electroplating industry. Although no occupational illness has been documented for electroplating operators, they are routinely exposed to hazardous substances known to cause serious health problems. The use of cyanide, generally considered the most potentially dangerous of the electroplating chemicals, is carefully monitored and employees are trained to use it properly. Combining employee education with substitution of less toxic chemicals may provide the least costly and most productive control of workplace hazards. Replacing cyanide plating solutions with

noncyanide baths is strongly recommended.

#### **Economic Comparison**

When the R/R system is installed on the ANC line, the economic benefits become significant. An economic comparison for the change to ANC and then for that change plus the addition of the R/R unit is provided in Table 1. An annual cost savings of \$14,000 is achieved by switching from a CN to an ANC process with a savings of \$62,000 when the R/R system is also added to the line; this savings takes into account the annual cost of operation of the R/R system which is \$10,900.

Making the switch from CN to ANC requires disposal of the existing 1,800 gal CN bath at a cost of \$20/gal for a total cost of \$36,000. This must be calculated as part of the capital investment for this

project. Adding the R/R system increases the capital investment by \$51,822 for a total of \$87,822. These capital investments and the operational expenses listed in Table 1 were entered into a spreadsheet program that calculates a number of economic indices. The calculations were based on 1992 costs. They use an inflation rate of 4%, a discount rate of 7.7%, a depreciation schedule of 7 yr, and a project life of 10 yr. It was assumed for all calculations that the line operates 8 hr/day, 5 davs/wk for 50 wk/vr. Table 2 contains the results of the spreadsheet calculations. This analysis shows the recycling option provides the greater economic benefit, the shorter payback period, and the larger return on investment.

#### Discussion

As a normal part of a plating line, a rectifier is used to convert alternating cur-

Table 1.	Comparison of Annual Operational Costs for CN Process, ANC Process without R/R Unit, and ANC Process with R/R Unit at P&H Plating
	Co.

Process Operation	CN Costs (\$)	ANC Costs (\$)	ANC + R/R* Costs (\$)
Bath makeup	1771	1860	1860
Bath maintenance	22325	21225	19425
Water usage			
1. Use @ \$7.56/7480 gal	1213	1213	364
2. Sewering @ \$5.59/7480 gal	897	897	269
Wastewater treatment			
1. Cyanide oxidation	14000	0	0
2. Metal precipitation	69000	69000	20700
3. Labor @ \$15/hr	7500	7500	2250
Sludge disposal @ \$209/yd³	2600	2600	1820
Total	119306	104295	46688

\* Assumes 70% water and 30% zinc hydroxide recycled

#### Table 2. Comparison of Economic Indices for the Alkaline Noncyanide Plating Process with and without the Recovery/Recycle System

Index	Option		
	ANC	-,	ANC + R/R
Capital Investment	\$36,000		\$87,822
Payback Period	3 yr		1.5 yr
Net Present Value	\$57,500		\$281,122
Implied Rate of Return	27.0%		71.9%

rent to the direct current needed for the plating process. Some type of cooling is needed to prevent the rectifier parts from overheating and thus damaging or destroying the entire unit. The rectifier on the test plating line is cooled by water although air-cooled models are used on other zinc plating lines at P&H. Tap water used in this noncontact cooling system is not discarded but is rather added to the counter flow rinsewater tanks on the plating line. Because of this continuous addition of fresh water to the plating line, a holding tank to collect the R/R treated water was installed. Water in this tank can be used in the rinsing operation and as makeup water for replenishing the plating bath. The tank is designed with an overflow valve that opens and sends excess water to P&H's wastewater treatment area for further treatment before discharge. Although this means that the objective of zero discharge has not been met and that this precipitation process is partially serving as a pretreatment step, the company estimates that the amount of water from this line that needs treatment has been reduced by more than 60%. Additionally, the cost of the precipitation pretreatment is less than would be the cost of pretreating the cyanide containing rinsewaters. The compliance criteria that need to be met by the final treatment are only those for zinc, since there is no longer cyanide in this rinsewater. The maximum discharge levels for metals are generally easier to achieve than are those for cyanide. This results in reduced treatment costs and fewer compliance problems.

The recovery efficiency for zinc hydroxide from the CNT system averages 84%; however, because of the variability in the numbers and types of plating jobs and the general fluctuations in business (all of which play a role in the amount of zinc hydroxide needed for the line), the company does not recycle all of the precipitate that is recovered. Additionally, the recovered zinc hydroxide is not a totally suitable substitute for the zinc ingots traditionally used to add zinc to the plating bath. All of the precipitate produced is passed through the filter press, which

greatly reduces its volume. A portion, which varies depending on production needs, but generally averaging 30%, is returned to the plating bath. The remaining 70% is stored for later use or disposed as a hazardous waste. While it would be possible to petition to delist this waste, the amount being produced is less than 5% of the metal waste that the company produces and must routinely dispose. Since much of the other metal waste was from cyanide-based lines and probably contained residual amounts of cvanide, even after treatment, it was disposed as a hazardous waste. Currently, it is more economically advantageous to simply add the zinc hydroxide to that waste and dispose of it as hazardous rather than separating it, storing it, and applying for delisting.

The company has recently converted all of its plating lines from CN-based to ANC-based. This change will eliminate the need for cyanide destruction in the company's treatment operations, will eliminate one potential compliance problem, will eliminate the potential health risk associated with cyanide exposure, and will ultimately save the company money. The change was completed more quickly than originally anticipated. Now that it is complete, it may become more economically inviting to pursue the delisting process for the zinc hydroxide that isn't being recycled. Also, the elimination of the cyanide lines will allow use of the precipitated zinc hydroxide to replenish other zinc plating baths, which is an option currently under consideration at P&H.

### Conclusions And Recommendations

The CNT-designed R/R system proved quite successful in meeting the project objectives. By converting from a CN-based to an ANC-based plating bath, the company eliminated one step from the treatment cycle, i.e., the destruction of cyanide. The removal of cyanide from the system also reduced the risk to employees by eliminating a highly toxic substance from their work environment. The purification of the wastewater proved so successful that nearly all of the recovered water could be recycled as well as much of the precipitated zinc hydroxide. As a result of installing this recovery unit, annual operational costs (including treatment and disposal costs, raw material purchases, and water usage fees) were reduced by \$62,000. The costs to design and install a R/R system like the one in use at P&H Plating is recovered during the first year and a half of operations. Additionally, recycling of the recovered materials reduced water usage and discharge by 841,911 gal and reduced the sludge disposed by 14 yd<sup>3</sup>/yr. These savings apply to a single line, but the test unit could easily accommodate a second line's waste, which would double these waste reduction figures. This system is simple and functions well. It is in use at P&H Plating today, and its use in similar electroplating operations would result in economic benefits comparable to those described in this project summary.

Finally, there are still many pollution prevention opportunities for the electroplating industry left to explore. Documented case studies of process modifications and technology evaluations that lead to source reduction are available, but more are needed. Distribution of this information to the appropriate audience can be achieved with the assistance of trade groups for the electroplating industry. Continued association with these industry organizations is essential to identify new pollution prevention options and to promote adoption of those that have proven successful. This continued interaction can only benefit all parties involved. Economic benefits could be substantial to companies willing to work toward source reduction. The environmental benefits that could result from the reduction in toxicity and volume of this industry's wastes would be significant and would be reason enough to continue to support research that will bring about those reductions.

The full report was submitted in partial fulfillment of Cooperative Agreement #CR815829 by the Hazardous Waste Research and Information Center under the sponsorship of the U.S. Environmental Protection Agency.

Jacqueline M. Peden is with Hazardous Waste Research and Information Center, Champaign, IL, 61820. **Paul M. Randall** is the EPA Project Officer (see below). The complete report, entitled "Alkaline Noncyanide Zinc Plating and Reuse of Recovered Chemicals," (Order No. PB94-205549; Cost: \$19.50, subject to change) will be available only from: National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650 The EPA Project Officer can be contacted at: Risk Reduction Engineering Laboratory U.S. Environmental Protection Agency Cincinnati, OH 45268

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