

The discharge limits on toxic substances, such as cyanide, are getting tighter and tighter every year. Zinc platers—especially shops using barrel plating equipment have the most difficulty meeting the strict discharge limitations. Although chloride and alkaline zinc bath formulations have gained wide acceptance, cyanide solutions are still used in many specialized plating operations.

T his is a case history of a plating job shop in Muncie, IN, which has been in the zinc plating business for more than 26 years, and now specializes in highthickness zinc plating. There is a very good market for heavy zinc plate; however, plating solutions using cyanide formulations have proven most successful.

Wastewaters are treated in a conventional chromium reduction, cyanide oxidation (alkaline chlorination) metal hydroxide precipitation system. High cyanide readings first started to plague the company when ascorbic acid was added, to preserve the effluent monitoring samples. Making matters more difficult, the high readings were sporadic and had a "roller coaster" pattern from day to day. We used an "investigative study" approach to pinpoint the problems, so process changes could be implemented to prevent future pretreatment permit excursions.

A Background

This "job shop" plater has built a reputation for high-quality rack and barrel zinc plating. Because non-cyanide solutions have not yet been successful in plating high-thickness zinc-especially parts that are crimped or bent after plating—cyanide zinc formulations are still used.

The shop employs about 50 to 60 people and generates between three and

four million dollars in annual sales. Zinc plating is done on two automatic rack plating machines, using both a programmed hoist and a return-type conveyor. There are also two hand-operated zinc barrel lines in operation.

In 1989, a brand new, automated, continuous flow-through wastewater treatment system was purchased and installed. The equipment is designed to process 60 GPM and uses a conventional metal hydroxide treatment process. Hexavalent chromium is reduced to the trivalent state with sodium metabisulfite, and cyanide is oxidized in a two-stage, alkaline chlorination process, using sodium hypochlorite. The trivalent chromium- and cyanide-free wastestreams are neutralized with sodium hydroxide (pH 9.2), coagulated with ferrous sulfate, and flocculated with an anionic polymer. The wastewater is then clarified in an Inclined plate gravity settler and discharged to a publicly owned treatment works (POTW).

The underflow, or sludge, is pumped from the clarifier into a holding tank for "thickening." Some of the sludge is also fed back into the neutralization reactor, to "seed" the flocculation process and maintain an optimum suspended-solids content. Periodically, sludge is withdrawn from the thickening tank and dewatered in the filter press. The sludge is then shipped to a treatment, storage and disposal (TDS) facility, where it is rendered Ton-hazardous.

Muncie's POTW is rated at 24 milliongallons-per-day (MGD). The pretreatment program is part of the Bureau of Water Quality. Typical pretreatment permit limits are shown in Table 1.

Industry has enjoyed a good working relationship with the Bureau for the past 20 years, in part because the Director of the Bureau expects all surface finishers to operate according to the

Table 1 Pretreatment Permit Discharge Limitations							
Regulated Parameter Cadmium	Daily Maximum (mg/1) 1.2	Four-Day Average (mg/1) 0.7					
Chromium	7.0	4.0					
Copper	4.5	2.7					
Cyanide To	1.0						
Lead	0.6	0.4					
Nickel	4.1	2.6					
Silver	1.2	0.7					
Zinc	4.2	2.6					
pН	5.5-10.0	N/A					
Oil & Grease	40.0	N/A					
*TTO	N/A	N/A					
*No TTOs used at this facility							

See Part II, Section VI: TTO Requirements.

same set of rules. Out-of-compliance situations are not tolerated and the city is quick to use enforcement actions that may include stiff fines. Prompt enforcement action has saved shop owners from being sued by third parties, who have had a "field day" in many midwest communities. Besides, the Municipal Waste Treatment Plant has its own problems. The plant already has had to do one toxicity reduction evaluation (TRE) study, and is now running biomonitoring tests.

The Investigative Plan

The objectives of our investigation were to first find out if the high readings were truly caused by cyanide's getting into the effluent. Once this was done, our investigation would focus on isolating the problems and making process changes, to ensure that the conditions

Table 2 Cyanide Aging Tests					
Retention	Total				
Time (Hrs)	Cyanide (mg/L)				
0	2.70				
3	2.60				
6	2.20				
9	1.40				

Table 3 Effluent From Second-Stage **Cvanide Reactor** Total Amenable Solution CN (mg/L CN (mq/L) Raw Sample 54.80 72.10 Filtered Sample 1.63 3.17 Coagulated, Flocculated, Filtered 0 14 0.25

Table 4 **Cvanide Concentrations** In Process Tanks Total Amenable Process CN (mg/L) CN (mg/L) Barrel Soak 90.0 90.0 Cleaner Chromate 41.6 40.0 Bright Dip

could not recur. Our investigative plan was built around these three major premises:

- 1. Analytical errors
- II. Incomplete cyanide oxidation process
- III. Infiltration

The heart of our study consisted of extensive and very costly analytical laboratory testing for free and total cyanide. All conclusions and recommendations would be based on empirical data, obtained from our laboratory tests. Also, pilot tests would be run in the laboratory to confirm our findings before any new equipment purchases or process modifications would be implemented.

Our first group of tests was designed to make certain that cvanide, indeed, was present and that there had been no "false positive" results caused by interfering reactions. The next series of tests focused on checking the effluent from the cyanide reactors, to ascertain the efficiency of the two-stage alkaline chlorination process. The third, and most comprehensive testing program included sampling all the tanks in the plating lines for free and total cyanide. This was done, to identify possible sources of cyanide that could infiltrate into the effluent. The lastand most costly-tests included sampling the effluent for nearly one month.

The Investigative Process

The first area of investigation was to check for analytical errors. In order to confirm that cyanide was truly present on occasion, in our effluent, we began a daily sampling schedule, where a "grab sample" was pulled at the same time, each production day. As outlined in 40 CFR 403.12, Subsection B-5iii, a 250 mL sample of effluent was drawn every 15 minutes, for a total of 1,000 mL (four *samples*). A waste treatment operator's log was also started, with specific instructions that he or she document everything that had happened with the equipment and processes during the shift, and make special notations if batch dumps (spent cleaners, chromates) were being treated.

Most of the samples were collected in triplicate and properly preserved with sodium hydroxide and ascorbic acid, then refrigerated. Because the high cyanide readings were sporadic in nature and only occurred intermittently, we suspected the problem may have been analytical error. Specifically, when testing for the presence of cyanide at the 1 mg/L level, many interfering ions, such as sulfur, can give a false positive test. However, having different laboratories and using different testing methods on the same sample would enable us to verify that cyanide was, indeed, present. Furthermore, "aging" tests would be conducted, to see if longer retention times would allow residual "free" chlorine to completely destroy the cyanide over a period of several hours. Although we also could have used biomonitoring tests to confirm the presence of cyanide, the cost of such a method is prohibitive.

Our second area of investigation centered around checking the efficiency of our alkaline chlorination process. We had assumed that all the cyanide was being oxidized to cyanate, because our effluent showed a positive test for free chlorine. But cyanide readily combines with soluble iron, to form very stable "ferrocyanide complexes," which are commonly called "Prussian Blue." So, additional laboratory tests were performed, to determine if ferrocyanide complexes were present and could be broken down and/or precipitated from our effluent.

The last area of the investigation included extensive laboratory tests, to find possible sources where cyanide could infiltrate into waste streams that were not treated by alkaline chlorination. Unfortunately, the ubiquitous cyanide ions can be quite elusive and difficult to isolate. So, in order to be sure we had not overlooked any possibility, we sampled every conceivable tank, including metal cleaners, chromates and even acid pickles.

Findings of the Investigation

The results of split samples analyzed by different laboratories, using different methods, showed good agreement. Also, the laboratories had good quality-control documentation, including spiked sample recovery and statistical analysis, using statistical process control (SPC).

In addition, we theorized that, if cyanide were truly present, residual chlorine should oxidize the cyanide and reduce the concentration over time. Therefore, we analyzed some "aged" samples that were not preserved with ascorbic acid. (Ascorbic acid reacts with the residual chlorine and prevents cyanide's oxidation during the sample holding period.) Table 2 shows results of this study.

Laboratory tests on the effluent from our two-stage alkaline chlorination process gave us some most-interesting data: Cyanide was not being completely destroyed in the reactors.

The data in Table 3 clearly show that the suspended solids in the reactor tanks contain a large amount of cyanide. Also, even though the effluent gives a positive test for residual chlorine, cyanide may still be present as complexed ferrocyanides. Additional laboratory tests did confirm the presence of iron in our waste streams, and ferrocyanide in the reactors. Fortunately, we were able to precipitate the ferrocyanide complex from the solution with the coagulation, flocculation, and clarification processes.

The data from our comprehensive tank sampling program indicated that cyanide was infiltrating into waste streams that were not being treated by alkaline chlorination. As table 4 shows, cyanide was found in some very unusual places. *We* have tabulated only the most severe cases, though most of the tanks sampled contained at least 1 mg/L of cyanide.

Although it would have been nice if "analytical error" had been the cause of our problems, such was not the case. The data dispelled any belief we had that interfering reactions had caused "false positive" tests for cyanide.

Table 5											
Date 1992	Alkaline Cone.	Chromate Cone.	Multivariable Filter Backwash	e Correlatio Neut. pH	n Study 593/520 Running	CN- Total	Zn	Fe			
3/5	No	Yes	Yes	9.7	Yes	2.36	.29	1.70			
3/6	No	Yes	Yes	—	No	0.53	—	—			
3/9	No	No	Yes	9.6	No	0.58	.56	.80			
3/10	No	Yes	No	9.2	Yes	0.06	.97	.43			
3/11	No	Yes	Yes	9.3	No	0.66	.50	.95			
3/12	Yes	Yes	No	9.4	No	1.36	.92	.39			
3/13	No	N o	Yes	9.2	No	2.09	.45	1.70			
3/1 6	No	No	Yes	9.4	No	0.71	.65	1.10			
3/17	No	No	Yes	9.3	Yes	1.94	.48	.30			
3/18	No	Yes	Yes	9.3	Yes	0.45	.69	.50			
3/1 9	No	Yes	Yes	9.3	No	0.05	.32	.41			
3/20	No	No	Yes	9.3	No	2.40	.35	1.40			
3/23	No	No	Yes	8.9	Yes	0.47	.90	1.20			
3124	No	Yes	Yes	8.9	Yes	0.10	.69	.54			
3/25	No	Yes	Yes	8.8	No	0.10	1.50	.38			
3126	No	Yes	No	8.8	No	0.33	.66	.63			

We came to realize that our twostage alkaline chlorination process does not-operate at 100 percent efficiency. These data explain why cyanide shows up in our sludge from the waste treatment process, during the toxic characteristic leaching procedure (TCLP) test. Obviously, if there is cyanide in the sludge, it was not completely destroyed in the treatment reactors. Also, because the sludge contains iron from the coagulation process, additional "iar tests" are being conducted to find a new coagulant that does not contain iron. This is necessary because the backwash from the sand filters may contain floe that is coagulated with ferrous sulfate. This backwash is then treated in the alkaline chlorination process, so we would rather not put iron into the cyanide-bearing waste stream.

In addition, cyanide was infiltrating waste streams that were not being treated by alkaline chlorination. Our data indicated a positive correlation between high cyanide readings and cleaner or chromate dumps.

Changes To Prevent Future Excursions

Cyanide was found primarily in the cleaners, chromates and sludge. Because of this, we prepared a two-phase "cyanide examination plan." Phase One addressed milestones that were easy to reach. For example, projects involved mostly plumbing changes and could be done quickly. Phase Two involved the purchase of additional waste treatment equipment and major plumbing modifi-, cations that would be accomplished over a 90-day period.

Within 30 days, both the major Phase One milestones were achieved:

- 1. All cleaner rinsewaters were plumbed to the cyanide treatment system.
- 2. Spent cleaners were pumped into the emergency storage tank for alkalies and "batch" treated with high test hypochlorite (HTH), before being bled into the cyanide treatment system.

The second phase of the project was completed within 90 days:

1. Multi-media sand filters were installed to "polish" the effluent. The backwash, which was mostly fines and "pin floe," and may contain small amounts of cyanide, was collected in the alkaline emergency storage tank and bled into the cyanide treatment system.

Cyanide "Roller Coaster" Persists Nothing is more frustrating than to think you have the problem solved, just to see it reoccur. Management wanted assurance, before more capital was invested in additional waste treatment equipment, that the problem would, indeed, be resolved. We suspected that the high cyanide levels were caused by incomplete precipitation of ferrocyanides. If this were true, there should be a direct correlation between iron and total cyanide, and an inverse relationship between cyanide and zinc. This would occur because the cyanide was complexed with the iron, and precipitated with zinc sulfate.

More laboratory tests were in order. Again, an effluent sample was pulled at the same time each working day for almost a month. The conditions during the shift were monitored for such activity as treatment of concentrated chromates, or backwashing of the sand filters. Each sample was analyzed for total cyanide, iron and zinc. The results of these tests are shown in Table 5.

As we studied the test data, we found that the predicted correlations were true. Most of the days with high total cyanide levels also had high iron and low zinc readings. Also, toward the end of the test, we tried lowering the pH of the neutralization reactor. Because iron precipitates at a lower pH, we theorized that more ferrocyanide could be removed if the pH were lower. This theory was also supported by the test results.

We confirmed our suspicions that our problem was being caused by the incomplete precipitation of complexed ferrocyanides. Other factors—treating chromates, backwashing sand filters, or plating high drag-out parts-did not seem to have a bearing on the high cyanide levels. Before investing any more capital, we decided to try "fine tuning" the reactors to maximize precipitation of the ferrocyanides. This first step was to determine how far we could lower the pH in the neutralization reactor and still get good metal removal. Historically, we had neutralized at a pH of 9.2 to 9.5, which seemed optimal for the precipitation of chromium and zinc. Laboratory tests indicated that the pH could be lowered to 8.5 without reducing the efficiency of the zinc and chromium removal process. Much to our surprise, this fine tuning was all that was needed to completely eliminate the "roller coaster" effect we had been experiencing with occasional high cyanide levels in the effluent.

Cyanide: Handle With Care

Cyanide, one of the world's greatest completing agents, may be found in cleaners, chromates and sludge from the waste treatment process. In order to remove cyanide to levels of less than one mg/L in the effluent, care must be taken to make certain that all process tanks and their associated waste streams that contain cyanide are properly treated. Moreover, monitoring the alkaline chlorination process for residual chlorine does not guarantee that the process is working properly. This is because the sludge from the reaction process may also contain complexed ferrocyanides. Because this sludge may be carried into the effluent, it must be removed with polishing filters. Also, backwash from the polishing filters may contain cyanide and must be properly treated.

In addition, cyanide can exist in chromate baths. In fact, ferrocyanides are sometimes added to proprietary products used for chromating aluminum to accelerate the conversion coating process. Consequently, if spent chromate baths are contaminated with ferrocyanide, care must be taken to precipitate the complexed cyanide in the neutralization reactor. The pH should be operated as low as possible and still get good metal removal.

Under no circumstances should reduced chromium be introduced into the alkaline chlorination process. This is because trivalent chromium may be deoxidized to the hexavalent state. Hexavalent chromium easily "slips through" conventional hydroxide precipitation metal removal processes and shows up in the effluent. Then, instead of chasing the elusive cyanide ions, you will be hunting for chromium ions, which can be just as difficult to catch !•

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