Advice & Counsel

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Manufacturing TRI Trouble

Dear Advice and Counsel,

We recently had an inspection by a representative of our regional office of EPA. He informed us that our TRI report was deficient, because we had failed to report that we manufactured approximately 90,000 lb of copper cyanide in 1995. He says this was caused by reaction of the sodium cyanide with the copper anodes that we purchase. Is this guy for real?

Signed, Just a Plater

Dear Just,

He's for real, all right. Making a determination of reportable quantities for Toxic Release Inventory (TRI) reporting can be quite a confusing effort. While it may seem strange to be considered in the "chemical manufacturing business," when you look at the process details, that is exactly what is going on in the plating solution while you are plating.

AESF addressed the determination of reportable substances, including the "manufacture" of reportable compounds within a plating solution (using a cadmium plating solution as an example) back in 1991, at our first Regulatory Compliance Workshop. The section on determining reportable substances is reproduced here.

Determination of Reportable Substances for Sample Plating Co.

Most of the chemicals used at Sample Plating Co. are purchased on a regular basis in shipping containers of 55 gal or less. The chemicals are bought frequently enough that the purchases and use of the chemicals are effectively the same. Upon reviewing the purchase records for calendar year 1990, it was found the the following items were purchased in significant quantities:

Sulfuric acid	70 drums
Chromic acid	32,000 lb
Chromate 349	2,500 lb
Black chromate #11	3,000 lb
Cadmium anodes	27,500 lb
Cadmium oxide	200 lb
Sodium cyanide	21,200 lb
Nitric acid	40 carboys

In addition to chemicals used at the facility, the company must also consider non-ferrous parts that were finished on-site. A review of major jobs handled during the year for clients showed that 1,000,000 pieces of a stainless steel part, weighing about one-quarter lb, were polished and passivated. The part was made from 410 stainless steel.

Each of the items was then reviewed to determine which substances were reportable. The reviews follow.

Chromium Compounds

Use of chemical: Chromate conversion coating of cadmium-plated parts and decorative chromium plating. (This falls under the category of "Process the chemical—as an article component" by EPA definitions.)

Trade Name	Quantity (lb)
Chromic acid	32,000
Chromate 349	2,500
Black Chromate #11	3,000
TOTAL	37,500

Note: The entire weight must be used for chemical compounds, not just the percent Cr.

This is greater than the 25,000 lb exemption level, therefore, *this is a reportable substance.*

Chromium (metal)—processed as solid mixture in 410 stainless steel articles

Use of chemical: Polishing and passivation of stainless steel parts. (This falls under the category "Process the chemical—as an article component" by EPA.)

Metal	Quantity (lb)
410	250,000

% Cr	Quantity (lb Cr)
12.5	31,250
TOTAL	31,250

This is greater than the 25,000 lb exemption level. We may now check to see if an article exemption would apply. The article exemption as currently redefined by EPA basically says that if a substance is processed as a shaped part and does not have a release of the *substance being reported*, the processing is exempt from reporting.

Processing the stainless steel parts results in the following types of chemical releases:

- To the POTW: Releases of chromium compounds, but no releases of chromium (metal).
- To the air: A small release of particulates containing chromium (metal) that will round to zero under EPA guidelines.
- To the land: A small release of buffing dust from the air cleaning device that contains chromium (metal). Note: The chromium present in the wastewater treatment sludge contains chromium compounds, not chromium (metal).

Because there are releases of chromium metal to the air and land from the buffing operation, the article exemption does not apply. If we did not have the buffing operation, the current EPA definition of article exemption would apply to the processing of the stainless steel parts, because there are only releases of

chromium compounds, not releases of chromium (metal). This is, therefore, *a reportable substance.*

Under EPA rules, we may choose to file one report as chromium compounds for both the chromium compounds and the chromium (metal).

Cadmium (metal)

Use of chemical: Cadmium plating of parts. (This falls under the category "Process the chemical—as an article component" by EPA.)

Metal	**Quantity (lb)**
Cadmium anodes	27,500

This is greater than the 25,000 lb exemption level. *This is, therefore, a reportable substance.*

Cadmium Compounds

Use of chemical: Cadmium plating of parts; additions of cadmium oxide to the bath. (This falls under the category "Process the chemical—as an article component" by EPA.)

Metal	**Quantity (lb)**
Cadmium oxide	200

Generation of cadmium cyanide in the bath: Under redefinitions issued by EPA, even though the cadmium anodes have been counted as cadmium metal, the cadmium cyanide produced from the anodes in the bath must also be counted, because it falls into another category of "cadmium compounds." (This falls under the category of "Manufacture the chemical—produced for on-site processing" by new interpretations of the definitions by EPA.)

The actual amount of cadmium cyanide may be estimated based on the atomic weights:

Cadmium anodes x 164/112 = cadmium cyanide manufactured
27,500 lb x 1.46 = 40,150 lb

This is greater than the 25,000 lb exemption level, therefore, *it is a reportable substance*. Under EPA rules, we may choose to file one report as cadmium compounds for both the cadmium compounds and the cadmium metal.

Cyanide Compounds

Use of chemical—Cadmium plating of parts. (This falls under the category of "otherwise used" by EPA.)

Compound	**Quantity (lb)**
Sodium cyanide	21,200

This is greater than the 10,000 lb exemption level, therefore, *this is a reportable substance*.

Note: Generation of cadmium cyanide in the bath—the cadmium cyanide generated from the sodium cyanide in the bath is not counted, based on EPA interpretations.

- The sodium cyanide in the plating bath forms another cyanide compound, cadmium cyanide. If we included the cadmium cyanide, we would be double-counting the cyanide ions present as compounds. In a similar way, we could even triple count by including any iron cyanides formed during plating. We should only count the original compound containing the cyanide toward the threshold determination to prevent multiple counting, based upon EPA interpretations.
- This is a different condition than the generation of cadmium cyanide (cadmium compound) from a cadmium anode (metal) in which the cadmium ions are being counted in different categories, but are only being counted once in each category.

Nitric acid

Use of chemical: Passivation of stainless steel parts. (This falls under the category of "otherwise used" by EPA.)

Trade Name	**Quantity (lb)**
Nitric acid* 42 Baume	6,000
Chromate 349**	2,500

Percentage	**Quantity (lb Nitric Acid)**
67.18 %	4,030*
25 %	625**
TOTAL USE	4,655 lb.

**For passivation 40 carboys @ 150 lb.*
*** As part of the proprietary chromate.*

This is less that the 10,000 lb exemption level, therefore, *this substance is exempt*.

Assuming all of the nitric acid used by Sample Plating Co. was converted to sodium nitrate, through neutralization (in wastewater treatment), and assuming your company used sodium hydroxide for neutralization, the total "water dissociable nitrate compounds" manufactured by your wastewater treatment system can be calculated from the chemical equation:

$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

Nitric acid has a molecular weight of 63, while sodium nitrate has a molecular weight of 85. That and the equation means for every 63 lb of nitric acid neutralized, you manufacture 85 lb of sodium nitrate. Put in another way, each lb of nitric acid yields 85/63, or 1.35 lb of sodium nitrate. Because Sample Plating Co. used a total of 4,655 lb of nitric acid (per our earlier calculation), the total sodium nitrate manufactured was $4,655 x 1.35 = 6,280 lb, which is below the 25,000 lb manufacture threshold for reporting.

Let's assume, however, that you exceeded the manufacture threshold. The release you report is not the total sodium nitrate we just calculated. It's just the amount of nitrate *ion* released. We calculate the amount (%) of nitrate ion in sodium nitrate by dividing the molecular weight of nitrate by the molecular weight of sodium nitrate:

62/85 x 100 = 72.95 %

The release of nitrate ion is the total amount of sodium nitrate produced multiplied by 0.7295.

Platers using cyanide plating solutions should almost always be marking:

a. Produce
c. For on-site use/processing
e. As a byproduct
… in section 3.1 of EPA Form R
P&SF

Reference: EPA 745-R-95-002 "List of Toxic Chemicals within the Water Dissociable Nitrate Compounds Category and Guidance for Reporting."

Author's note: Thanks to Joelie Hill, Chair of the AESF RCA/CERCLA Committee, for reviewing the information in this article, and for suggestions regarding it.