



Advice & Counsel

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Manufacturing Trouble (Again)

Columnist's Note: We recently have received so many calls from metal finishers concerned about numerous metal finishers' receipt of violation letters from the U.S. EPA, indicating that thousands of dollars of fines are due because the company failed to report or consider the manufacture of nitrate compounds in its past Toxic Chemical Release Inventory Reports (Form R), by the simple neutralization

of nitric acid in a wastewater treatment system, that we have decided to interrupt our "Training Columbo" series to submit the following article, which describes a typical phone call.

Dear Advice & Counsel,
I have just received a letter from the EPA indicating that they want to fine me a total of \$25,000 for five years' worth of Form R reports

that did not contain information on my manufacturing nitrate compounds. I am not a nitrate compound manufacturer, nor do I want to be. I have not been able to get any help from the hot line on this. What is going on here?

Signed,
Joe Plater
(Not Joe Manufacturer)

Dear Joe (Plater *AND* Manufacturer), Unfortunately, the EPA considers you to be a manufacturer, even though you do not produce nitrate compounds. You actually produce nitrate ions, but so far, the EPA has not accepted this difference. Therefore, until they are successfully challenged, you will need to make a determination of whether you exceed the reportable quantity of nitrate compound manufacture, which currently is 25,000 pounds.

The EPA requires each company using nitric acid—either as an acid or in chemical solutions, such as chromates—to determine the amount of “nitrate compounds” that are manufactured when the acid is neutralized (assuming it is neutralized) in your wastewater treatment system.

You need to review all of your MSDSs on chemical products you purchase for the presence of nitric acid. If a product contains nitric acid, determine the maximum it contains, or contact the supplier to obtain a concentration estimate (request this in writing). If it contains less than one percent nitric acid, you don’t need to include it in your estimation. Be sure

“Manufacturing” Processes

Process	“Compounds Manufactured”
Zinc Phosphating	Zinc compounds
Nickel Plating	Nickel compounds
Addition of Zinc Chloride to Zinc Plating Tank	Zinc compounds
Addition of Zinc Oxide to Zinc Plating Tank	Zinc compounds
Addition of Cadmium Oxide to Plating Tank	Cadmium/Cyanide compounds
Addition of Gold Cyanide	Cyanide compounds
Metal Plating, Soluble Anode (any type)	Metal compounds
Chromium Plating (Lead Anodes)	Lead compounds (chromate)
Chromium Plating (Lead-Antimony Anodes)	Lead/Antimony compounds
Alloy Plating	Metal compounds related to the alloy
Silver Plating, Soluble Anodes	Silver/Cyanide compounds
Addition of Silver Cyanide to Plating Tank	Silver/Cyanide compounds
Stripping a Metal	Metal compounds
Neutralizing Nitric Acid	Nitrate compounds
Precipitation of Iron Cyanide (waste treat)	Cyanide compounds
Acid Pickling a Listed Metal	Metal compounds
Chromating Zinc	Chromium/Zinc compounds
Electropolishing	Metal compounds (depending on which metal is electropolished)

to verify the nitric acid content, based on 100-percent nitric, or adjust for water content. For example, if a chromate supplier says he adds 10 gallons of nitric acid for every 100 gallons of chromate, is that 10 gallons

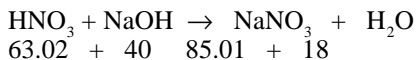
of 70-percent nitric acid (30% water) or 10 gallons of 50-percent nitric (50% water)? Nitric acid always contains some water, usually around 30 percent, but it may be more or less dilute than that. In the end, you want

to have the gallons of 100-percent nitric acid (no water) to make your calculation of nitrate compounds produced.

Once you have the above information, adjust each acid used for water content, total up all of the adjusted nitric acid you purchased during the reporting year, and subtract the amount that ended up in inventory at the end of the year. Also subtract any nitric acid that was sent off-site for disposal by commercial waste treatment facilities, if any. The acid sent off-site also needs to be adjusted for water content before you make the adjustment. The remaining nitric acid is subject to a calculation of the amount of nitrate compound manufactured. To make this calculation, we have made the following assumptions:

1. The total acid used for the year was 1,500 gal
2. All of the nitric acid used was 30-percent water (specific gravity 1.4)
3. The acid was neutralized with sodium hydroxide

The neutralization reaction is:



Each pound of nitric acid produces $85.01/63.02 = 1.35$ lb of sodium nitrate, or "nitrate compounds." Using the above information, you first multiply the gallons of acid by 11.67 to obtain the number of pounds of acid neutralized. Then multiply this number by 0.7 to adjust for the water content of that acid.

Example: 1,500 gallons of nitric acid was neutralized.

$$1,500 \times 11.676 = 17,514 \text{ lb}$$

$$17,514 \text{ lb} \times 0.7 = 12,260 \text{ lb of acid neutralized}$$

Based upon the neutralization reaction above, the 12,260 lb of nitric acid would produce $12,260 \times 1.35$, or 16,551 lb nitrate compounds.

Notes:

1. If calcium hydroxide is used for neutralization, each lb of nitric acid produces 1.30 lb of nitrate compounds. If you use a neutralizing agent other than sodium hydroxide or lime, contact a chemist to give you an alternate factor.
2. You are also manufacturing nitrate compounds by reacting nitric acid with metals in solutions, such as

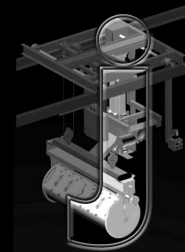
bright dips, chromates, and any other process where nitric acid dissolves a metal or smut. An analysis of the spent solution would allow for an estimate of these nitrate compounds.

3. The cutoff for manufacturing is 25,000 lb. In the above example, therefore, nitrate compounds need not be reported, but you should keep your determination on file so you can prove you made the calculation. If you can't prove you have made the calculation (during an inspection), be prepared to get a letter such as the one our writer above received.
4. If you do exceed the 25,000 lb manufacture cutoff, you must include nitrates in your TRI report, *but* you have the option of reporting only the nitrate portion of the release. In other words, when we calculated nitrate compounds manufactured, we calculated it as sodium nitrate. When we calculate the release for the TRI report, we have the option of reporting either sodium nitrate or just the nitrate (no sodium). To get just the nitrate, multiply any release of sodium nitrate by 0.73.

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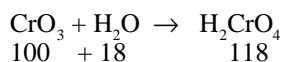
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5. A detailed guide to the nitrate issue was published by the U.S. EPA in 1996 as EPA 745-R96-004, and is available from: USEPA (7408) Washington, DC 20460.

Now, while we are at it, you really need to look at every process tank in your shop and determine what compounds are produced by that process. You can get help from your supplier, consultant, or from the EPA. As an example, if you add chromium trioxide flakes to water, they produce a chromium compound (chromic acid). The reaction is:



For every pound of chromium trioxide added to water, 1.18 pounds of chromic acid is produced. Take all the chromium trioxide flakes that were added to your chromium plating tanks and multiply the pounds by 1.18 to arrive at the manufactured pounds of chromic acid. (Note: some call chromium trioxide flakes “chromic acid” by mistake. It is not chromic acid until you add it to water.)

In this column, we have previously provided guidance regarding the EPA’s determination that a plating tank may be a manufacturing tank, if the anodes dissolve to form reportable compounds. EPA has decided that **all** the theoretical compounds that can possibly be formed must be considered and estimated in total. You’ll need a textbook to make this determination.

For example, *in theory*, when copper cyanide is added to an aqueous solution containing cyanide, or when a solid copper anode dissolves into a cyanide copper plating solution, a cyanide compound generally believed to produce $\text{Cu}(\text{CN})_3^{-2}$ ions is “manufactured,” by EPA’s determination. Further, according to EPA, because technical sources, such as *Modern Electroplating* (edited by Fredrick A. Lowenheim, third edition, John Wiley & Sons, Inc.), indicate that $\text{Cu}(\text{CN})_2^{-1}$ and $\text{Cu}(\text{CN})_4^{-3}$ could also be produced, EPA requires that the entire addition of copper cyanide be calculated as if it formed each of these ions independently, and then all of this production must be added together for the total manufacture of

copper compounds. Of course, you also need to determine if you exceeded the manufacture of **cyanide compounds** by anodic dissolution and by the addition of copper cyanide to the tank.

While the list in the accompanying chart is not exhaustive, it does illustrate some other “manufacturing” processes to consider.

If all of this sounds somewhat silly, because in many cases, there is no “net” manufacture of anything other than a solid metal coating, the silliness stops when the letter from EPA in the mail asks for a \$25,000 (in some cases much higher) “donation.” Efforts to date to convince EPA that this is an unfair burden, that the “compounds” are really “ions,” and that it creates a completely unrealistic picture to the community surrounding a metal finishing facility, have so far failed to produce any changes in the requirement.

Now is a good time to go over each Form R you have filed and make certain it contains the correct information and that your records of cutoff determinations are within easy reach upon an inspection. P&SF