TSCA CDR Byproduct Examples from the Printed Circuit Board Industry

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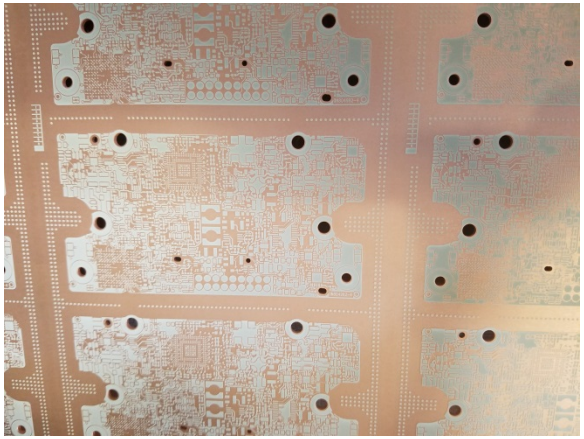
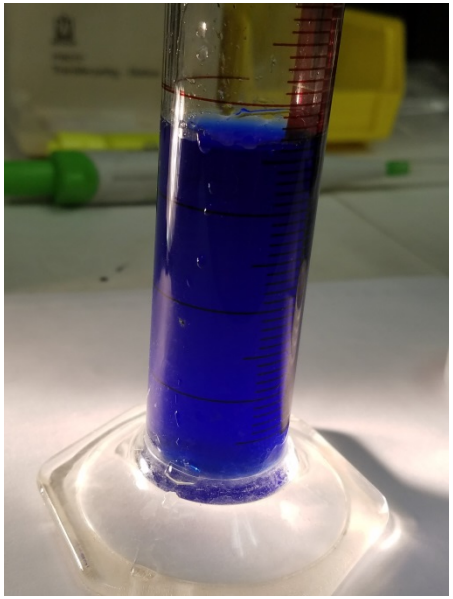
Background

- Prior to the removal of the exemption for reporting inorganic chemicals, printed circuit board manufacturers were not subject to CDR.
- Inorganic chemicals were assessed as low risk, low priority, chemicals.

Example 1 – Ammonium Chloride Etch

- Metallic copper is exposed to a mixture of ammonium chloride and ammonium hydroxide.
- Typically, about 1.18 lbs copper/gal is dissolved into the etchant at a final pH of 8.5-9.
- Etching defines the trace & pad patterns of the circuit board.
- As with many chemical etching processes, an excess of etchant is created as replenisher solution is added to control metal concentration, free chloride levels, pH, and specific gravity.





Example 1 – Ammonium Chloride Etch (cont.)

- Chemical suppliers and recyclers originally identified the etchant as a mixture of copper chloride and ammonium chloride.
- In the mid 1990's, some recyclers began to require identification of the solution as "copper tetraammine dichloride" on shipping manifests.
- When the TSCA inorganic reporting exemption was lifted, a PNM had not been filed for copper tetraammine dichloride.

- A simplified description of the chemical reaction is:

$$2Cu^{0} + 2Cu^{+2}(NH_3)_4Cl_2 \rightarrow 4Cu^{+1}(NH_3)_2Cl$$

- Whereas the regeneration reaction is:

$$4Cu^{+1}(NH_3)_2Cl + 4NH_3 + 4NH_4Cl + O_2 \rightarrow 4Cu^{+2}(NH_3)_4Cl_2 + 2H_2O$$

- We're unaware of any test methods that directly measure copper compounds that might theoretically be inferred from the component formulation. Certain scholarly articles propose that several other compounds may exist in the chemical matrix in a shifting equilibrium based upon component concentrations, ORP, and pH.

Example 1 – Ammonium Chloride Etch (cont.)

- The components exist in ionic form. Precise quantification of compound ratios is unknown. Atomic Absorption (AA) analysis provides an accurate measurement of the amount of copper in the etch solution. Weights of copper compounds must be extrapolated based upon a comparison of their molecular weights.

- For instance (assuming 1.18lbs/gal copper):
  - If $Cu^{+2}Cl_2$ - Multiply copper wgt. by 2.116 , 10,041 gal > threshold
  - If $4Cu^{+1}(NH_3)_2Cl$ – Multiply copper wgt. by 1.274, 16,636 gal > threshold
  - If $4Cu^{+2}(NH_3)_4Cl_2$ – Multiply copper wgt. by 1.547, 13,695 gal > threshold
  - If $Cu4(NH)_4Cl_2$ (CAS No 10534-87-9) –
    Multiply copper wgt. by 3.190, 6,652 gal > threshold
  - Or, submit a PMN and report as a UVCB.
    25,000 lbs (threshold) / 9.81 lbs/gal = 2,549 gal

Example 2 – Wastewater Treatment Sludge

- Product rinsing generates wastewaters containing traces of heavy metals (primarily copper), ammonia, ammines, EDTA, citrates, oxidizers, along with sulfuric, hydrochloric, and nitric acids.

- These require pretreatment prior to discharge to remove heavy metals and meet pH limits. A variety of chemical processes are used to remove copper to below permit discharge limits including:
  - Neutralization with lime or sodium hydroxide to form separable copper hydroxide precipitates.
  - Reduction with sulfide or thiocarbamate compounds to reduce metals associated with ammonia, EDTA, or other complexing agents.
  - Addition of metallic iron or aluminum to prompt metal cementation.

- The resulting solid precipitates are combined into a filter cake and dewatered. The filter cake can be landfilled or shipped to smelters for copper recovery.

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Example 2 – WWT Sludge (cont.)

- WWT filter cake typically contains more than one copper compound depending upon the wastes treated and treatment processes used. These may include metallic copper, copper hydroxide, copper sulfides, copper sulfates, copper nitrates, or copper oxides.
- As with ammonium chloride etchant, while copper content can be easily determined, precise quantification of various compounds may be extremely difficult.
  - If Cu(OH) - Multiply copper wgt. by 2.116, 10,041 lbs Cu > threshold
  - If CuS - Multiply copper wgt. by 1.274, 16,636 lbs Cu > threshold
  - If CuO - Multiply copper wgt. by 1.547, 13,695 lbs Cu > threshold
- If UVCB – report if 25,000 lbs of filter cake is generated.

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Ensuring TSCA Compliance

- Essentially there are two choices:
  - Identify reportable compounds, or
  - Report the entire volume of etchant or filter cake as a UVCB.

  (Note: A PMN would be required to register the UVCB onto the TSCA Inventory, possibly for each generating facility, due to differences in treatment methods and chemicals used.)

- Which approach is correct (legally defensible)? EPA guidance was published Feb. 2016 and states that either approach is "potentially" appropriate. However, EPA's enforcement branch has not committed to be bound by the guidance.

Other Considerations

- Reporting is largely duplicative. Copper values in etchant and filter cake are already provided to EPA annually through ERCRA/TRI reports, along with recycler addresses, EPA ID numbers, and processing codes.
- Materials do not pose significant health hazards and have not been priorities for evaluation by TSCA.
- Potential worker exposures are very limited, typically no more than 4-6 employees per facility
- The materials are not widely distributed in commerce. (~ 4-6 facilities in the US)