Advice & Counsel



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Mail Call

Recently Received Communications to "Advice & Counsel"

Dear Advice & Counsel,

Regarding your *P&SF* article on circuit board wastewater treatment, there are other more cost effective and environmentally friendly (they go hand-in-hand) methods. Here is a quick list of concepts:

- 1. Assume that there is no tin-lead plating and lead from hot air leveling is segregated from all other waste streams. Also assume that water volume reduction is prerequisite and at a practical minimum.
- 2 Collect all copper bearing rinse water plus non-oxidizing, <1,000 mg/L copper contaminated, <15% TDS process solutions for pH control (3.5)



- 4.5) and then treatment by copper selective ion exchange (aminodiacetate functional groups get up to 2 pounds Cu/cu.ft.). Sulfuric acid regenerant is simply "spiced up" for plating out the copper into a recyclable solid.

- 3. There usually are three different groups of spent process solutions requiring various types of batch treatment. A key is to take advantage of RCRA exclusions, exemptions and conditional exemptions to minimize counted hazardous waste. Some of the treatment procedures can include pretreatment prior to copper stripping by the ion exchange system.
- 4. Instead of adding a second filter press, add a much cheaper and space efficient sludge thickening tank. The tank will thicken <0.1% solids to near 0.5 - 1%solids and significantly reduce the number of cycles on the one press.
- Eliminate the precoat's waste volume by adding polymer to the thickening tank that is fitted with a slow mixer.
- 6. Circuit board wastewater is on the oxidizing side and hinders normal treatment methods. Ferrous sulfate provides both reducing and coagulating effects (simple color changes are a shop level bonus) but significantly adds to the waste volume. Sodium bisulfite is useful in batch applications. The use of DTC is expensive, usually indicative of too much water usage and other methods will work better.
- 7. If the shop must go through the costs of design and permitting, it may be more cost effective to cancel their permit and go to zero discharge. I did one for a circuit board shop 25 years ago and it worked well for 20 years. I also have a recycle system operating at a chemical miller for almost 15 years

and couple plating shops for nearly 10 years. The chelating scare in apply ion exchange to circuit board rinse water is unfounded. Ammonium and chloride complexing doesn't significantly occur below 1% concentration.

8. It isn't clear to me why mixed bed IX is proposed. If lead is properly segregated, there is no need for anion exchange. Also, mixed beds are intended for low TDS input and very low TDS effluent. A two bed cation/ anion would meet the limits and be much more efficient.

Your suggestions on IX filtration and initial bypass of the press are right on. Regarding chelate treatment, adjustment to pH 2 is certainly safe but most dissociate below pH 4 - 4.5. Gosh, this got too wordy and I need to get back to work (zero discharge citric acid passivation line).

Greg Allan, P.E. Advanced Chem. Tech.

Dear Mr. Allan,

Thank you for your in-put. You make some excellent points and with your permission I have published your response.

Dear Advice & Counsel (via copied e-mail to Mr. Steve Andrews, EU Department of Trade & Industry)

Mr. Andrews,

I am seeing claims in various publications that "hexavalent chromium", in its metallic state (electroplated), is zero valence, and therefore RoHS compliant. In Mr. Altmayer's article in the March, 2005 issue of *Plating and Surface Finishing* he states:

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"Electroplated chromium (decorative and hard) is a metal and, therefore, is in the zero-valent state (as are all metals). The European ELV Directive does not ban any chromium in the zero valent state."

Our electroplating suppliers are also making this statement/claim for the RoHS Directive. Common sense would dictate that the EU would not ban hexavalent chromium in its "non-metallic" state. This is a critical issue for our company. A "GREAT DEAL" of effort is currently being expended to eliminate COMPONENTS ELECTROPLATED USING THE hexavalent chromium PROCESS from our products.

My question specifically is: "Is a component, electroplated using the hexavalent chromium process RoHS compliant because, in its electroplated/metallic state, the chromium plating is zero valence?"

George

Mr. Andrews replied and copied the author as follows:

Thank you for your email. The Directive restricts the presence of hexavalent chromium (CRVI) in end-products (covered within the scope) to 1ppm or 0.1% by weight in homogeneous materials. Currently, the only approved exemption for hexavalent chromium is in its application as an anti-corrosion of the carbon steel cooling system in absorption refrigerators. **The Directive does not restrict trivalent chromium or other forms of chrome** (emphasis added).

Hope this helps. You will find more guidance on the RoHS Directive on our web site at http://www.dti.gov.uk/sustainability/ weee/index.htm

Best wishes, Steve Andrews Department of Trade & Industry/SD 1 4th Floor 151 Buckingham Palace Road London SW1W 9SS Tel: +44 (0) 20 7215 1670 Fax: +44 (0) 20 7215 5835 Email: steven.andrews@dti.gsi.gov.uk Website: www.dti.gov.uk/sustainability

Dear Advice & Counsel,

I recently took the electroplating and surface finishing class you taught in St. Louis, and I was wondering if you could give me some advice.

I have a Ni Strike tank (Sulfamate Ni Strike) that is out of spec low for pH. I let the bath run overnight thinking that should naturally increase the pH but it didn't seem to. I have checked the anode basket connection for corrosion and didn't find anything there. For the

Ni Plate baths, if we are out of spec low for pH we add Ni Carbonate. Is it okay to add this to the strike tank also to raise the pH? I also am having out of spec high for HCl and tried adding water to the tank last night and this morning. I am again out of spec high for HCl, any suggestions? Based on this information, is the bath actually considered to be a Ni Sulfamate strike? Do you see any potential risk of running with high, out of spec HCl in this bath? I would like to try a Wood's Ni strike in place of what we are using in an attempt to improve the Ni adhesion to the stainless steel, maybe I should also try an actual Ni Sulfamate strike also then. Thanks again for your time, I really appreciate it.

Signed, Woody

Dear Woody,

Adding nickel carbonate to raise the pH is fine and there should be no problem. I'm not sure I understand the comment about high HCl, as a sulfamate nickel strike typically does not contain hydrochloric acid. It is made with sulfamic acid. If you have a Wood's nickel strike with high HCl, that would make sense, and I would not worry about it. But, if the specification requires a correction, the same nickel carbonate will do that as well.

I have two formulations for a sulfamate nickel strike:

Nickel Sulfamate	40 oz/gal
pH (adj with Sulfamic Acid)	1.5
Boric acid	4 oz/gal
Room Temp., 20–100ASF	

The above looks to me like what you have, except there is no hydrochloric in it. What you have may be a proprietary formulation. Running high in HCl typically poses no problem unless the acid is so high that the nickel deposited is porous or too thin. Another sulfamate formulation in my database is:

C. 16	
Suffamate Nickel Str	ike:
Nickel Sulfamate	320 g/L
Sulfamic Acid	150 g/L
Temperature:	50°C
Current Density:	50 ASF
A Wood's Nickel stri	ke formulation is:
Nickel Chloride	30 oz/gal
Hydrochloric Acid	8 fl oz/gal
Room Temperature	
Current Density	100-300 ASF

Dear Advice & Counsel,

My question is simple; does a black chromium deposit contain hexavalent chromium?

Signed, Blackie

Dear Blackie,

I cannot answer this question definitively, because there are dozens of black chromium plating formulations, and perhaps the one that you are using produces some hex-chrome in the deposit.

From a theoretical standpoint, it is highly unlikely that a black chromium process contains enough hexavalent chromium to fail the RoHaS intitiative. Most black chromium deposits are black because of the presence of oxides of chromium in the deposit, but according to my chemistry handbook, the oxides that are black in color do not contain hexavalent chromium. For example CrO is black, but the Cr is +2 valent. Cr_2O_3 is also black-grey and the chromium is +3 in valence. CrO_2 is black, and the Cr is +4 valent. The oxide that contains hex-chrome CrO_3 is red-purple, not black. You have a couple of options:

- 1. Talk to the chemical supplier who sold you the solution and find out if they have any information.
- 2. Test some plated parts.

Since the solution that black chromium is plated from contains hex-chrome, there is always the chance that some hex chromium is trapped in the deposit. In my opinion, the amount trapped would not cause a failure of the test. But to be sure, it is best to do the test. *P&SF*



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