

Tech Talk

Fine Lines in High Yield (Part CLXI)

Some Health and Effluent Disposal Considerations in PWB Fabrication

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Tech Talk, to the best of my recollection, has never addressed the topic of workers' health and effluent disposal issues facing the PWB industry. This is not surprising since the theme "Fine Lines in High Yield" has no direct links to these important issues. However, the new restrictions on the permitting process of new PWB facilities in China, driven by environmental considerations, highlight the importance of these questions and warrant a closer look.

Plating, Surface Finishes, Desmear.

Acid copper plating baths typically have been agitated by so-called air sparging, a process in which air is pumped into the bath, exiting through holes in a sparger manifold as small bubbles next to both surfaces of the racked boards. When these bubbles arrive at the surface they cause the formation of sulfuric acid aerosols that constitute a health hazard, especially by interfering with what is called "tracheobronchial mucociliary clearance". There are engineering solutions to avoid worker exposure to these aerosols, but a more elegant approach that also offers several technical advantages, is the use of eductors, i.e. submerged jets that move the plating solution.

Electroless copper has been under scrutiny for many years, a factor which has contributed to the introduction of direct metallization processes. One issue is the health concern about using formaldehyde as a reducing agent. Ventilation of these baths and monitoring for acceptable exposure levels has allowed the continued use of electroless copper based on formaldehyde, but suppliers have developed formaldehyde-free baths as an alternative where local formaldehyde regulations present a problem. Another concern is the use of EDTA complexing agent in electroless copper baths, e.g. in European countries where the discharge of aqueous effluent containing EDTA is prohibited because EDTA affects the ability to remove heavy metals from the waste streams. For some years, suppliers have been offering electroless copper baths that are EDTA-free.

Immersion tin baths typically use thiourea to complex cuprous ions to shift the immersion electron exchange reaction in favor of the reduction of Sn^{2+} to Sn^0 . Thiourea was found to cause cancer in animal studies and was found to be teratogenic in rats. Thiourea may also interfere with waste treatment of heavy metals. For these reasons, baths containing thiourea are typically treated with oxidizing agents before disposal to chemically degrade the thiourea.

Today, desmear of drilled holes uses permanganate oxidant. The use of chromic acid has completely disappeared, in part because of concern about the carcinogenic affect of hexavalent chromium.

Solids Disposal/ Recycling

Packing materials and scrap laminate are typical solid waste components generated by PWB fabricators. The proper disposal of such solid waste, or mandatory recycling, is governed by local, state and federal regulations. In Germany, for example, suppliers of packaged items are required to take back the packaging material. The so called "end caps" of dry film resist packaging are often returned to the supplier for re-use. Some dry film resist "packaging" actually does not use "packaging" other than shrink-wrapping, eliminating the need for boxes. The cores and end pieces form an interlocking structure like Lego® pieces, forming a pallet-sized cubicle. There have been innovative approaches to recycling scrap laminate and circuit boards. I reported on a unique process operated by Fuba in Germany (Ref. 1) that employs a combination of techniques to separate and recycle the components of scrap boards. All materials, metals, glass fiber and



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resin, find a new use after proper separation – there is no residual waste stream. The separation methods employed are mechanical size reduction and classification, magnetic and electrostatic separations. The separated materials find new uses as flame retardant building materials, as paving material, or park benches, to name a few. The metal fraction is sent to a smelter for metal recovery and separation.

More recently, Hall and Williams (Ref. 2) reported on a process for material recovery from printed circuit boards. The boards were pyrolyzed at 800 degrees C in an oxygen-free atmosphere to yield easily separable fractions of metal, glass fiber, and volatile oils and gases.

Dry Film Photoresist Health and Effluent Disposal Considerations

Most dry film resists contain acrylate monomers that form polyacrylates during exposure with UV-light. These acrylate monomers are skin irritants (causing dermatitis), respiratory irritants, and sensitizers. Operators that come in contact with these monomers can develop a sensitization to acrylates, the severity of which differs widely between individuals. The skin rash that develops is quite similar to poison ivy exposure. Therefore, skin and respiratory exposure to acrylate monomers should be avoided. The monomers are found in spent developer solutions, around hot roll laminators, and to some extent around the exposure frame of printers during vacuum draw-down. When handling developer solutions the operator should be wearing protective gloves such as Neoprene gloves. Exposure units should be vented to the outside, as should be hot roll laminators and vacuum laminators. Laminator exhaust flow rate recommendations are typically in the range of 300 cfm (8.49 m³/min (high end) and 130 cfm (3.68 m³/min (low end). It should be noted that the odor of the resist, or any other material, is not proportional to the level of a harmful ingredient, and is therefore not a reliable indicator of safe or unsafe exposure levels. Another interesting observation we made was that the level of ozone measured that forms during UV-exposure, is very low and is not a cause for concern.

In addition to the photosensitive resist layer, the polyester base and the polyethylene cover sheet need to be disposed of. It goes without saying that the polyester foil is not suitable for home use as packaging material, especially as food wrap, because it has been in contact with the acrylate monomers in the resist. Polyester foil has been recycled for re-use in polyester by a process called alcoholysis. In this process, the polyester chain is cleaved into ethylene glycol and terephthalic ester, for re-use as building blocks for new polyester. This operation requires a large scale to be cost effective. Polyethylene can be recycled thermoplastically into shaped objects whereby the purity of the recycle stream is a consideration.

The disposal of spent developer solution and stripper solution is worth discussing in more detail which will be the subject of next month's Tech Talk. Highly alkaline strippers can attack the metal surface of the boards and cause build-up of copper, tin, and lead in the stripper solution. The spent solution should therefore be analyzed for metals before going to secondary waste treatment to assure compliance with in-coming water quality standards for such treatment facilities, e.g. POTWs (publicly owned treatment works). Disposal of spent developers and strippers in POTWs is not common on all regions of the world. It is common in the US but not in Japan where most resist waste is incinerated. This explains why resists developed in Japan typically form insoluble stripper skins to minimize organic content of aqueous waste for discharge to surface waters, but to capture most of the organic content for incineration. Conversely, generating aqueous waste streams with fairly high organic loads due to soluble or partially soluble stripper skins is not such a big issue in the US.

The dominant concern about the aqueous disposal and treatment of organic resist components is their biodegradability or compatibility with secondary waste treatment. Tests were run to demonstrate the compatibility of aqueous resist waste streams with biodegradation in secondary waste treatment (Ref. 3).

The bacteria of a waste treatment facility that feed on organic compounds in waste water are first "acclimated" over several weeks to a steady diet of spent resist being part of the organic food. This bacteria culture is then exposed to a food stream containing the new resist to be tested for compatibility with biodegradation. The test is conducted in a piece of equipment called Electrolytic Respirometer, that allows the accurate measurement of the oxygen uptake of the bacteria over several days, typically five days ("BOD₅"). The apparatus is a closed reactor (Fig. 1) in which oxygen is generated by electrolysis. The amount of oxygen generated, and consumed, is directly proportional to the amount of current used and is measured thereby. As oxygen is absorbed into the solution, it creates a partial vacuum. This causes a shift in the level of the electrolyte, the electrolyte touches the electrodes, current begins to flow, and oxygen is generated. As the pressure turns to atmospheric, the electrolyte solution shifts and no longer contacts the electrodes. The reaction products are CO₂ and "dead bugs" that have died of a natural cause after a long, happy life, sustained by non-toxic organics. The CO₂ generated in the reactor is adsorbed by alkali. Bacteria sludge generated in a waste treatment facility can be used as fertilizer.

Cumulative oxygen demand of the bacteria culture is then plotted versus time (see. Fig. 2). The green curve in Figure 2 shows the "base curve" oxygen consumption of an acclimated bacteria culture. If the oxygen consumption increases with the addition of the test resist, one concludes that the test resist is biodegradable. If the uptake is lower after the addition of the test resist, but oxygen uptake continues, one concludes that there is some degree of inhibition to biodegradation due to the presence of the test resist. If the oxygen uptake stops after the test resist addition, one has to conclude that the test resist is toxic. If the "base curve" does not shift at all after the addition of the test resist, one concludes that the new material is neither considered "food" by the

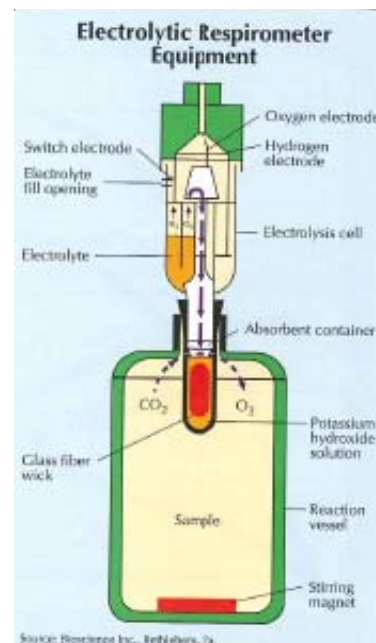


Figure 1: Electric Respirometer Equipment (Source: Bioscience Inc., Bethlehem, Pa)

bacteria, nor does it adversely affect biodegradation. Higher molecular weight acrylates fall into this category. If they are part of the sludge used as fertilizer, they will eventually degrade under the influence of heat, moisture and UV-light, just like Plexiglas.

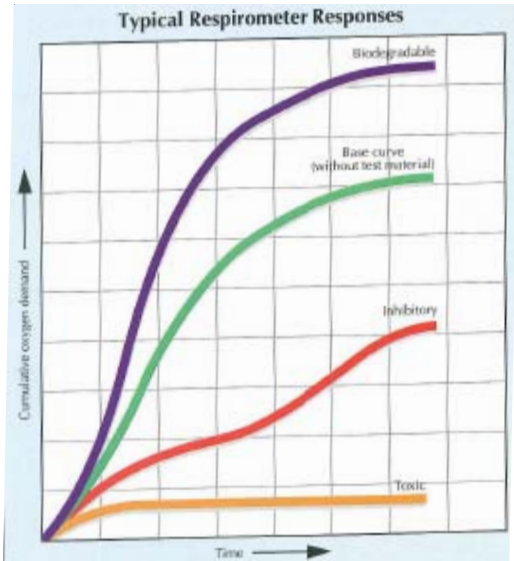


Figure 2: Cumulative Oxygen Demand Curves
(Source: Peter. S. Strilko)

References

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2. Processing waste printed circuit boards for material recovery, William J. Hall and Paul T. Williams, Circuit World, Volume 33, Number 4, 2007, pg. 43
3. Responsible Effluent Disposal, Peter S. Strilko, Pollution Engineering, January 1992