Tech Talk

Fine Lines in High Yield (Part CLXII)

Dry Film Photoresist Effluent Disposal Considerations

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The February 2009 Tech Talk column discussed a number of health and environmental considerations in connection with PWB fabrication. The proper disposal of spent developer and stripper solution and stripper skins was one of the issues which is looked at closer in this Tech Talk. For more details see also Reference 1.

Stripper Skins

Resist skins are filtered from stripper solutions to prevent redeposition during spraying of the stripper solution and clogging of spray nozzles and to prolong the life of stripping solution chemistries. To dispose of these skins as non-hazardous material, it needs to be first demonstrated that the skins are non-hazardous. "Hazardous wastes" are regulated by RCRA (Resource Conservation and Recovery Act) requirements. Of particular interest to resist users are two categories of waste. "Listed" wastes are non-specific as to their make-up, but are generated from specific processes. For example, F006 listed wastes come from electroplating "process" wastewaters and sludges. "Characteristic" wastes, on the other hand, are those having one of several characteristics: Ignitability, Corrosivity, Reactivity, or Toxicity Characteristic. Toxicity characteristic leaching procedure or TCLP has limits based on a test that determines the leachable amount of materials such as heavy metals in the waste.

The stripper skins are usually free of any metals that would cause them to fail the TCLP tests, but initial testing of stripper skins generated by a specific stripping process should verify this. A number of years ago, one EPA region interpreted the F006 definition of listed waste to include these skins but after some clarifying discussions, the EPA now allows the skins to escape the F006 definitions, if the following conditions are met:

- Plating or etching equipment is not contiguous with the stripper equipment
- Parts processed in the plating or etching equipment are rinsed and dried prior to entering the stripper
- The user must be prepared to demonstrate that skins do not fall under corrosivity (pH$\geq$12.5 or $\leq$2) or toxicity characteristics (TCLP).

Resist Process Solution Pretreatment

The waste streams from resist processing solutions and related chemistries should be segregated from other waste streams. Depending on the treatment alternative chosen, precipitation of the resist may not be desired. Lowering the pH below about 8 for most resists will cause the dissolved polymeric micelle-like structures to begin to precipitate, in some cases forming a sticky mass. Thus plumbing should avoid inadvertently mixing with an acidic stream. Likewise certain waste pretreatment filtration systems used to remove metals should not be exposed to these solutions, as the organic components often tend to clog the membrane. The filtration system supplier should be consulted.

After resist processing streams are segregated, decisions have to be made relative to the treatment or pretreatment of these solutions.

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Developer Solution

Table 1 shows the characteristics of typical spent aqueous developer solutions using the recommended developer chemistry. For aqueous developers, the copper concentration is generally low enough, that the developer solution can be metered into the final neutralization section beyond the plant's waste pretreatment system or neutralized separately and metered into the sewered streams. These solutions should be analyzed initially and if possible before each dump to insure that no metals have been dragged in. Care must be exercised in the rate of metering and the pH control of this step, since dropping the pH below 8, may result in some precipitation of the dissolved resist materials.

Table 1 - Characterization of Typical Developer Solution - Loaded

Resist	COD	BOD	TOC	Loading*	Copper**
Aqueous	15-22,000	2,500-3,600	2,000-2,800	12-13 msf/gal	<1 ppm

* Loading is measured as a volume of resist per gallon of solution, msf is mil square feet calculated as the number of square feet times the thickness in mils (0.001 in.).
** An average number determined independently of the other data.

In situations where the organic content of the waste stream must be reduced prior to disposal, the resist can be precipitated and filtered out. A good procedure for precipitating the resist is to slowly lower the pH using sulfuric acid and to add a precipitation aid. Table 2 gives a typical procedure and concentrations for a number of aqueous resists, filter flow rates and the resulting COD's (chemical oxygen demand).

Table 2 - Typical Precipitation Chemistry & Results

Loading in msf/gal	Procedure	Filter rate	COD mg/l (after)
12-13	H_2SO_4 to pH 4 + $CaCl_2$ (usually first)	6-45	2000-3800

Filter rate is in gallons per minute per square foot of filter using a 1-2 micron filter, usually using a filter aid.

Strippers

It is possible to meter the stripper into the final neutralization tank of the plant waste treatment system. This will depend on the metal concentration, what the permit discharge limits are and whether the COD or BOD (biological oxygen demand) discharge will exceed them (see Table 3).

Table 3 - Characterization of Typical Stripper Solution - Loaded

Resist	COD	BOD	TOC (total org. carbon)	Loading*	Copper**
Aqueous	10-25,000	2,500-4,500	1200-2400	18-19 msf/gal	$\leq$4 ppm

* Loading is measured as a volume of resist per gallon of solution, msf is mil square feet calculated as the number of square feet times the thickness in mils (0.001 in.).
** An average number determined independently of the other data. It is very dependent on rinsing in the previous process, length of use, and drag-in of any complexers.

Stripper solutions may requirement pretreatment before discharge because of copper concentrations. The copper concentration needs to be monitored and compared to the applicable regional discharge limits.

If the copper concentration is too high and the stripper inexpensive, then it is possible to use a feed-and-bleed mode. This renews the stripper solution slowly. It constantly removes the metal ions and they never reach levels high enough to require treatment. High metal concentrations are prevented and the waste is organic with only traces of metal ions. Feed and bleed is especially effective with proprietary stripper because it helps to keep the copper level low enough that autocatalytic etching does not occur and increase the copper concentration even more.

In this case cost of treating the metals must be considered versus the cost of the stripper solution, if feed-and-bleed is used. Using straight caustic solution will not complex the copper and have lower copper concentrations, but may attack solder plating more rapidly.

Proprietary strippers containing metal complexers may be used in circumstances where solder plating must be protected from caustic strippers, more rapid stripping is desired, or a shiny copper surface is desired. Copper concentrations for these strippers will be much higher (see Table 4):

Table 4 - Typical Metals (Concentrations) Found in Spent (Proprietary) Strippers (Ref. 2)

Metal	Concentration (ppm)
Copper	30-300
Lead	50-150
Nickel	5-10
Tin	5-20
Chromium	3-10

Where the organic and/or metal concentrations are too high for discharge, there are two choices. The solution can be pretreated in a batch treatment to reduce the organic strength (see conditions in Table 5) and then to precipitate the metals as insoluble complexes. Two metal-complexing materials often used to precipitate the metals (copper and lead) from process solutions are DTC (dithiocarbamate) and TMT-15 (trisodium trimercapto-s-triazine) The alternative to batch treatment for the removal of organics and metals is to have the solutions hauled away for incineration.

Table 5 - Typical (Aqueous, Caustic) Stripper; Precipitation of Organics- Chemistry & Results

Loading in msf/gal	Procedure	Filter rate	COD mg/l (after)
18-19	H_2SO_4 to pH 4 or 5	1-18	2000-4300

Filter rate is in gallons per minute per square foot of filter using a 1-2 micron filter, usually using a filter aid.

The particular chemicals, order and manner of their addition depend on the resists that are present in the stream. Care should be taken to maintain effective stirring and use slow addition of dilute precipitating materials. This will minimize the tendency of resist precipitates to form a gelatinous material. Proprietary resist treatment chemicals are being offered for the neutralization, precipitation, flocculation, and de-tackification of resist from spent stripper solutions, to form a readily filterable precipitate.

References

1. Cost Effective and Environmentally Responsible Management of Dry Film Resist Process Waste Streams, John W. Lott & Karl H. Dietz, North East Circuits Association, TechCon ’95, November 8-9, 1995, Chelmsford, MA
2. “Dry Film Stripper Additives: Impact on the Stripper Disposal Process”, John A. MacNeill, CircuiTree, November 1994, pg.62