Presented at IPC Printed Circuits Expo® 2002
www.ipcprintedcircuitexpo.org

Dry Film Resist Stripping from Overplated Lines

Martin Hill
E. I. duPont de Nemours and Company
Towanda, PA

Abstract
The ideal outer layer has a uniform circuit height throughout the board. This is a challenge to produce with pattern plating, because the plated metal height depends on the current density, which varies across the board, based on the size and proximity of features being plated. The resulting board typically has areas where the plating height is higher than desired (overplated), and can be particularly acute in areas of fine lines and spaces. In these areas, if the plating overlaps the top of the resist, then the resist is difficult to strip cleanly, and this can be the limiting factor in whether a fine line board can be made in production.

Clean stripping from overplated lines is an area of active research in our laboratories, and we would like to report the factors in resist design and processing that affect it, and recommendations for driving to finer lines and spaces in production.

The Mechanism of Development and Stripping
Dry film resists contain polymeric binders with acid groups, which react with the alkaline sodium carbonate developer solution to form sodium salts, and become soluble in water. This enables the unexposed resist to be removed from the copper board.

The resist also contains multifunctional acrylic monomers, which are cross-linked on exposure to UV light. Because the monomers are now connected by covalent bonds, the resist image is insoluble, and will not dissolve during development.

The primary active ingredient in the stripper is also a base, either hydroxide ion, or an amine, generally at a higher concentration than in the developer. This will also not dissolve the crosslinked monomer network in the image.

However, because of the stripper's higher concentration, basic ions can penetrate the resist surface and neutralize the acid groups to form salts inside the polymerized network. These salts are centers of high polarity, and water diffuses into the resist to solvate them. The influx of water swells the resist image and forces a dimension change. The dimension change stresses, and ultimately breaks, the adhesive bond between resist and copper substrate, and also breaks the resist image into pieces. The now detached pieces are free to be washed off the board by the spray action of the stripper and rinse.

The Impact of Overplated Lines
It can be quite difficult to pattern plate a circuit design with the desired uniform plating thickness across the whole board, particularly if there are large differences in feature sizes (e.g., line widths), because of the non-uniform current density across the board. So it is common to find the plated metal extending above the top surface of the resist: typically it also plates horizontally as well as vertically, forming a "mushroom" shaped cross-section. Figure 1 shows a 150-micron line/150 micron space pattern overplated in a copper-plating bath by 50% (i.e., 50% more plating time than that required to match the 38 micron resist height).

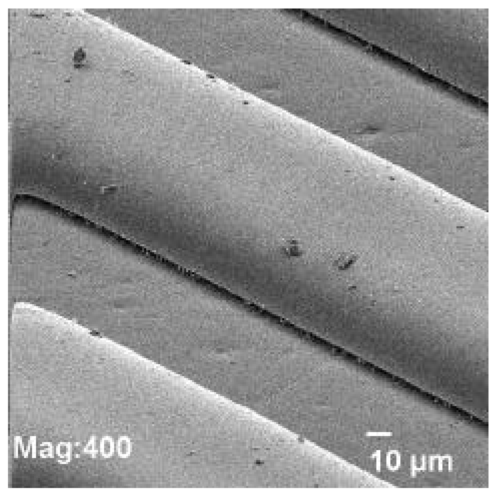

Figure 1 – Overplated Line/Space Pattern

The overlap of metal over the resist protects the edges of the resist from the mechanical action of the stripper sprays, and also from penetration by the stripping solution. Thus the resist strips much more slowly and incompletely from overplated areas of the board, especially in fine line areas. Even if the resist breaks up into particles, these particles are often trapped in the narrow confines of the plated lines, and cannot be removed by longer residence times in the sprays. Then in etching, the resist residues protect the metal underneath, and the finished board has shorts in the fine line areas.

Stripped Resist Particle Size

The traditional view, from where our studies started, is that one would logically expect resists that break up into small pieces would strip more cleanly from overplated lines. Thus resists have usually been evaluated by examining resist images with large solids (at least a centimeter square) and measuring the particle size as they strip. The finer the particles, the better, as long as they can be filtered from the stripper solution effectively and without plugging the filter media.

The interest has been in stripping resists from 75 micron spaces and smaller, and without over plating, many resists strip well from spaces of this size. If the stripped resist particle sizes are measured from large area images, the particles are in the 1/16 to 1/8 inch (1587 - 3175 micron) range. Thus the particle sizes measured are as much as forty times larger than the dimensions of the lines to be stripped. Thus stripping within the confines of plated lines must involve a different mechanism than stripping in a large solid area. So it was decided to develop a different test method that actually uses plated channels of the dimensions in which there is interest.

Stripping Cleanness Test Method

The test consists of imaging a series of equal width lines and spaces graduated from 20 microns in 10 micron increments up to 100 microns, and in 25 micron increments up to 150 microns, plating 1.5 times the resist height with copper, and measuring the amount of resist remaining between each set of plated lines after stripping. Copper plating was chosen (and not copper followed by tin or tin/lead) because it gives smo oth deposits, and is reproducible in plating height. Not surprisingly, the finest lines were very hard to strip, while the broadest lines stripped quickly and cleanly. So a plot of % resist remaining vs. line/space dimension shows an "S"-shaped curve as shown in Figure 2.

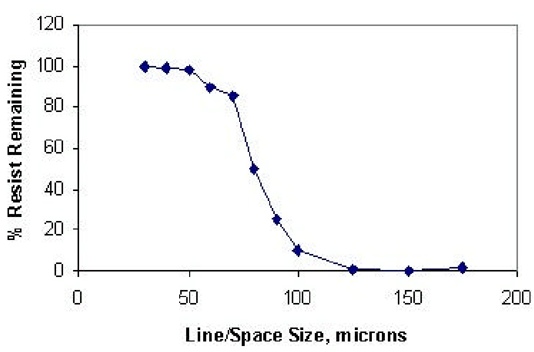

Figure 2 - Stripping Cleanness vs. Line/Space Width

The test has to be carefully controlled. It was found that the cleanness of stripping is very strongly dependent on the plating height, and therefore the amount of plating has to be carefully controlled.

Each board was weighted before and after plating, to get an overall view of how much metal is deposited, and SEM photos were taken of representative lines from each sample to ensure a smooth deposit, and the amount of mushrooming over the resist is consistent. It was also found that board placement in the plating rack affects the amount of plating, and hence the stripping results. Thus in making comparisons between resists or processing conditions, the results are either compared between boards in the same position in the plating rack, or averaged from a complete rack of boards for one parameter.

The effect of stripping in a stirred beaker of solution vs. a conveyorized stripper was compared, and it was concluded that although conveyorized stripping gives both faster and cleaner stripping than in a beaker, the relative ranking of resist types for cleanness was the same for both methods. See Figure 3.

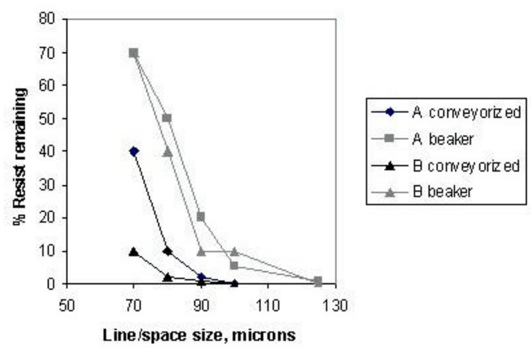

Figure 3 – Conveyorized vs. Beaker Stripping

It was decided to use the beaker in most tests, because it is a much more severe test, and helps to distinguish between variables more easily.

Comparing the stripping cleanness of several commercial resists, they could be ranked based on the cleanness plot.

Ranking: D (best) > B >> A=C

This ranking matched the experience with how these resists strip in customer usage. Thus, it could be confidently stated that the test produces realistic results, and the test was used to examine the effect of processing parameters on stripping cleanness.

The Effect of Exposure

It is known that the degree of polymerization increases with increasing exposure, and thus higher exposures produce more highly crosslinked materials.

This is not a linear effect; typically the degree of polymerization increases rapidly with exposure at first, but then levels off at high exposures, as monomer mobility within the material is more restricted by the increasing amount of cross linking. See Figure 4.

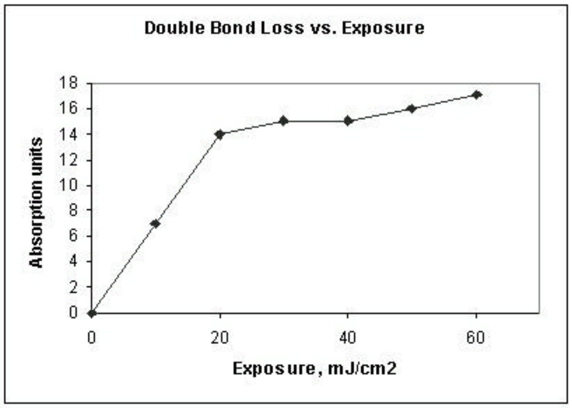

Figure 4 – Monomer Conversion vs. Exposure

This reduction of monomer mobility is paralleled by a reduction in permeability to stripper. Consistent with the observation that the monomer conversion levels off after an initial increase with exposure, stripping cleanness is slightly but not strongly dependent on exposure. See Figure 5.

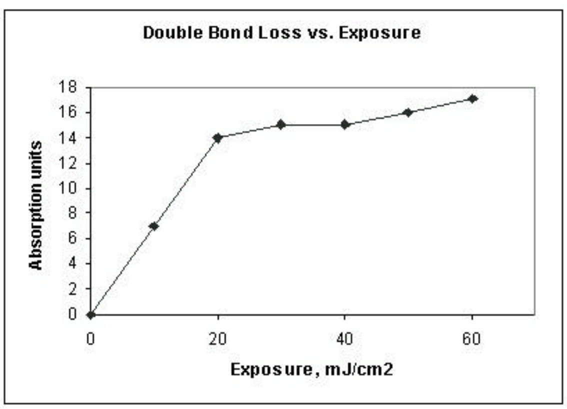

Figure 5 – Stripping Cleanness vs. Exposure

In addition, although the stripping time of unplated boards increased with exposure, with this degree of overplating, there was no effect of exposure on stripping time, i.e., the retarding effect of the barrier formed by the overplating overshadowed any effect due to exposure.

Stripping Speed

Since it was observed in the past that stripping in 3% sodium hydroxide vs. 1.5% potassium hydroxide gives faster stripping, but larger particle sizes, it would seem likely that formulations or conditions that strip the resist quickly would also promote cleanness of stripping. A number of resist formulations were compared which varied in stripping speed in non-overplated boards in this test. See Figure 6.

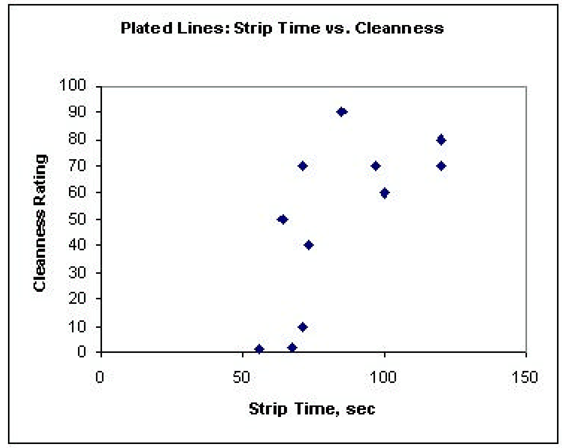

Figure 6 – Stripping Cleanness vs. Speed

While there is a general trend towards higher levels of stripping residues with slower stripping formulations, there are also samples, which stripped at the same time, but with major differences in cleanness, such as those stripping between 60 and 90 seconds in Figure 6. Thus stripping speed per se is not a determinant of stripping cleanness.

Particle Size

As mentioned before, the interest was in finding out how the particle size for resist stripped in a solid area would correlate with the cleanness of stripping in overplated lines. The same resists shown in Figure 7 were also exposed and developed to produce 25/50mm rectangular images and stripped. The particle sizes produced were:

Resist A	1-2 mm
Resist B	> 6 mm
Resist C	> 6 mm
Resist D	3-4 mm

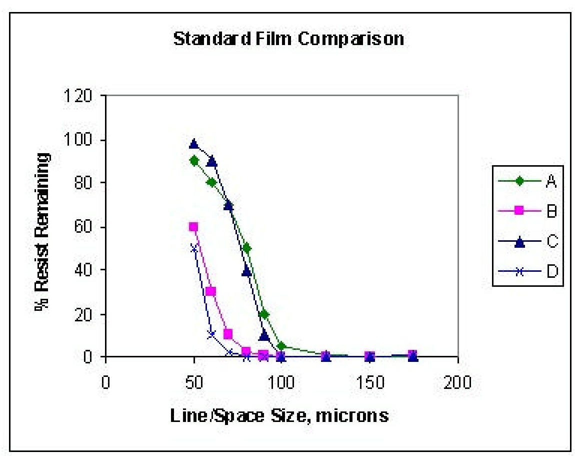

Figure 7 – Comparison of Standard Films

The ranking of stripping performance had D as the best, while its stripped particle size is intermediate between the others, and A and C equal to each other in stripping cleanness, but with the smallest and largest particle size respectively. Thus the particle size stripped from a developed image does not necessarily correlate to the cleanness of stripping in overplated lines.

Immersion Time in the Stripper

It would be reasonable to expect that if a resist is not completely stripped in a given time of immersion in the stripper; then leaving it in the stripper longer will remove more resist. However, it was found not to be true.

Stripping cleanness is not strongly dependent on the time in the stripper: once the resist is stripped, longer immersion does not clean up fine lines significantly.

Surface Preparation

Samples were prepared from vendor copper by brush scrubbing or by chemical cleaning (Atotech AFR-3/rinse/sodium persulfate etch 80 micro inches/rinse), and compared for cleanness of stripping. See Figure 8.

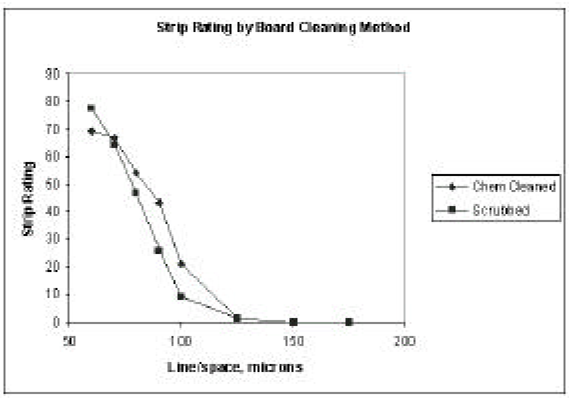

Figure 8 – Effect of Surface Preparation

Thus there is a small effect of surface preparation method on the cleanness of stripping.

This and the immersion time result indicate that the key determinant of stripping cleanness is what happens at the moment of release from the substrate. At that point in time, the stresses in the resist are at their maximum; the force of swelling by base and by water diffusing into the resist vs. the strength of the adhesive bond between resist and substrate. The cleaner stripping resists break away from the substrate before they disintegrate into particles, leaving a clean substrate surface.

Conversely, resists that leave residues can break up into layers before detaching from the substrate The top layers wash away all right, but the bottom layers stay on the copper surface. Since they are already swollen, there is no driving force to remove them from the copper, and they are unaffected by longer immersion times in the stripper.

Conclusions

The resist formulation and the process parameters both have a large influence on how cleanly the resist strips.

A tool now exists for comparing resist formulations and determining the formulation factors that affect clean stripping. Resists are being formulated that will incorporate this advantage.

The key process factors to pay attention to for clean stripping are:

1. Control plating height
2. Select a stripping chemistry using plated boards. Stripping speed and particle size of imaged boards does not necessarily correlate with stripping cleanness
3. Lower exposures are better, but the effect is small
4. Conveyorized stripping with good mechanical action gives cleaner stripping than tank stripping
5. Use a resist designed for clean stripping

Acknowledgements

The author would like to acknowledge Karl Dietz, Tom Foreman and Bill Pangratz for valuable consultations, and Sue Eicher and Pat Watkins for their excellent contributions to the experimental results.