Debonding of Photoresists by Organic Solvents

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SYNOPSIS

Chlorofluorocarbons (CFCs) have been widely used in the printed circuit board industry for many decades. However, the growing concern regarding their ozone depleting properties has demanded a ban on these solvents and consequently brought forth the search for environmentally friendly alternatives. In printed circuit board technology, methyl chloroform and methylene chloride have been widely utilized as solvents for developing and stripping, respectively, radiation sensitive materials useful in creating fine line circuitry patterns. The solubility of unexposed and exposed T168 resist in selected solvents or solvent mixtures at various temperatures is described here. Results addressing the ease of removal of such solvent based resists using environmentally friendly alternatives are presented. Debonding of the polymer layer from the underlying substrate was observed by monitoring the deflection of the composite strip immersed in the solvent using a Fotonic Sensor accessory. Debonding time, identified as the necessary time to remove the photoresist from such surfaces, can vary with temperature, solvent, photoresist type or thickness, and exposure energy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Photolithography plays a critical role in the art of printed circuit packaging by providing the capability of creating fine line circuitry patterns. Generally all photoresists include an organic resin binder, a photoinitiator or photosensitizer, and a reactive monomer. Optionally, they might also include organic or inorganic fillers, fire retardants, plasticizers, dyes, flexibilizers, thermal stabilizers, and other additives to improve the processing characteristics of the package. Depending on their composition, known photoresists are sensitive to UV radiation, X-rays, E-beams, or other sources of radiation that may be furnished to the resist through a pattern in a mask, such as an emulsion mask or chrome mask, by contact or projection, or a beam of radiation may be rastered. There are basically two types of photoresists: negative and positive. Normally in electronic packaging the positive resists are applied over a copper foil positioned on a substrate. After resist development, copper is etched from the unprotected

areas leaving behind circuit lines and features protected by radiation hardened resist. The hardened resist must then be removed. The negative resists are used when the circuit lines are provided by additive plating of copper, in areas where copper is desired, that is, electroless or electroless plus electroplating, rather than by etching of copper away from where it is not desired.

In processing negative working resists, unexposed areas of the imaged film are typically removed from the surface of a printed circuit board or substrate by action of a liquid developer in a spray form for a duration of several minutes or less. Depending on the particular type of photoresist composition, the liquid developer may be a simple organic solvent, an aqueous solution of an inorganic base, or a combination of organic solvent and aqueous base to form a semiaqueous developer.

Methyl chloroform (MCF) and methylene chloride (MC) are solvents that are widely used in electronic packaging and in other areas for developing and removing a number of photoresists that are otherwise resistant to chemical attack. Highly alkaline electroless copper plating bath used in additive processes, for example, typically provides a harsh environment for photoresists. In general, the more
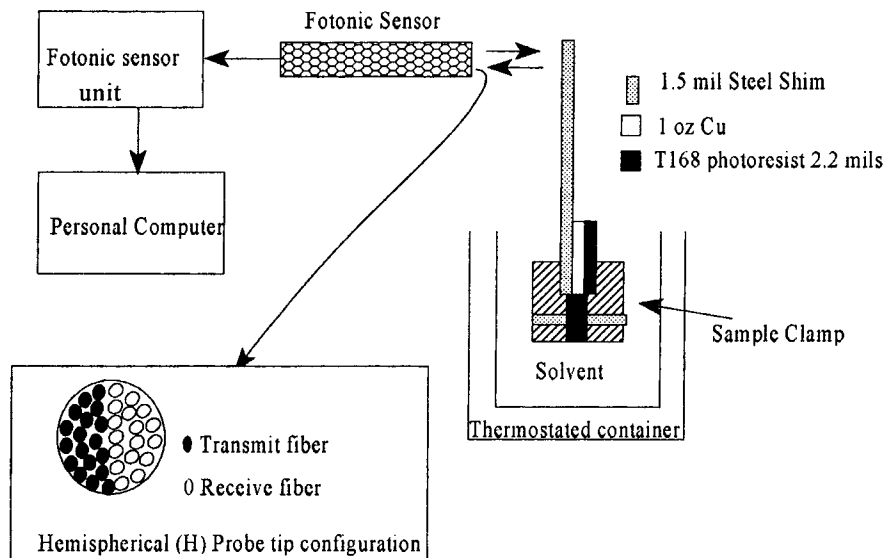
Figure 1   Schematic (side view) of the Fotonic Sensor accessory and probe configuration.

chemically impervious resists are removable in an organic solvent such as MC.[1,2]

Use of MCF developer is disfavored because of growing environmental concerns over the effect of gaseous halogenated hydrocarbons on the depletion of earth's ozone layer and concerns over introducing suspected carcinogens to the atmosphere. Several countries have set goals for their total elimination. However, there continue to be many manufacturing processes in which use of resists that are aqueously developable simply is not feasible. The industry therefore continues the search for an organic solvent developer as an alternate to MCF and photoresist stripper as an alternate to MC. The new solvents must meet specific manufacturing and environmental requirements with respect to flammability, toxicity, ability to effect dissolution, shelf-life, simplicity of composition, and compatibility with a spectrum of resists.

In our case Riston T168 photoresist is currently used in circuit packaging manufacturing to produce products by a fully additive plating method. Such photoresist having excellent resistance to alkaline media is removed from the circuit board in subsequent processing by the use of methyl chloroform (MCF) in the develop step and MC in the strip step simultaneously with the application of brushes in a horizontal stripper. Due to environmental concerns the use of MC along with other chlorinated solvents is undesirable.

The solubility of unexposed and exposed T168 resist in selected solvents or solvent mixtures at various temperatures is described here. Removal of the exposed resist from a laminate or copper surface can vary with temperature, solvent, photoresist type or thickness, and exposure energy. Results addressing the ease of removal of such solvent based resists using environmentally friendly alternatives will also be presented. Debonding of the polymer layer from the underlying substrate was observed by monitoring the deflection of a composite strip immersed in the solvent using a Fotonic Sensor accessory. Debonding time, identified as the necessary time to remove the photoresist from such surfaces, can vary with temperature, solvent, photoresist type or thickness, and exposure energy.

EXPERIMENTAL

Solubility Experiments

T168 solubility parameter determinations were made according to ASTM method D3132. The solubility classification was determined as soluble if the solvent appeared to have dissolved T168 to at least the same degree as MC and insoluble if less.

The experimental data were obtained according to the following method. A signal core was prepared by laminating two sheets of epoxy-glass prepreg between two 1 oz copper foils and a circuitry pattern was obtained on either side by photolithographic processes. On such a surface Riston T168 was hot

Table I   Solvent or Solvent Mixtures for Riston T168

Solvent (vol %)	Solubility Parameter δ	Hydrogen Bonding	Dipole Moment μ	Solubility Class
1. Diisopropyl ether	6.9	6.6	1.3	I
2. n-Heptane	7.3	2.2	0	I
3. Diethyl ether	7.4	6.9	1.2	I
4. n-Heptane/diisobutyl ketone (50/50)	7.6	3.7	1.4	I
5. Diisobutyl ketone	7.8	5.2	2.7	I
6. Diethyl ether/n-butyl acetate (57/43)	7.9	6.3	1.5	I
7. Cyclohexane	8.2	2.2	0	I
8. n-Butyl acetate	8.5	5.4	1.9	I
9. Cyclohexane/toluene (40/60)	8.6	3.2	0.2	I
10. Cyclohexane/benzene (50/50)	8.7	2.2	0	I
11. n-Butyl acetate/toluene (50/50)	8.7	4.6	1.2	I
12. EGMBE/n-butyl acetate (50/50)	8.7	6.2	1.8	I
13. Diethyl ether/2-ethylhexanol (33/67)	8.8	8.2	1.5	I
14. Toluene	8.9	3.8	0.4	I
15. 2-Butoxyethanol	8.9	6.9	1.6	I
16. Benzene	9.2	2.2	0	I
17. Propylene oxide	9.2	5.8	1.8	S
18. EGMBE/2-ethylhexanol (56/44)	9.2	7.8	1.6	I
19. Toluene/MC (50/50)	9.3	3.3	1.0	S
20. Toluene/dioxane (50/50)	9.4	4.8	0.4	S
21. 2-Ethylhexanol	9.5	8.9	1.7	I
22. Methylacetate	9.6	5.2	1.7	S
23. Methylene chloride	9.7	2.7	1.5	S
24. Dioxane/MC	9.8	3.7	1.1	S
25. Dioxane	9.9	5.7	0.4	S
26. Cyclohexanone	9.9	6.4	2.7	I
27. 2-Ethoxethanol	9.9	6.9	0	I
29. Dioxane/nitroethane (67/33)	10.3	4.8	1.5	S
30. Toluene/acetonitrile (50/50)	10.4	4.2	2.2	S
31. 50% EGMEE/n-amyl alcohol (50/50)	10.4	7.9	1.7	I
32. 2-Ethylbutanol	10.5	8.9	1.7	I
33. Dioxane/PCO3 (75/25)	10.8	5.3	1.6	S
34. Dimethylacetamide	10.8	6.6	3.8	S
35. EGMEE/methanol (80/20)	10.8	7.3	1.6	I
36. EGMEE/n-butanol (33/67)	10.9	8.2	1.7	I
37. Nitromethane	11.1	3.1	3.6	S
38. n-Butanol	11.4	8.9	1.7	I
39. Nitroethane/acetonitrile (50/50)	11.5	3.8	3.8	S
40. n-Butanol/DMF (67/33)	11.6	8.2	2.4	I

roll laminated and exposed to UV radiation. Coupons 2 × 4 cm in size, taken from such a signal core having the exposed T168, were subjected to various solvents at a range of temperatures between room temperature and 60°C in a test tube. The samples were agitated continuously either by hand or using a shaker. The time necessary to obtain a laminate surface, free from Riston T168 photoresist, is taken as the dissolution time, or time necessary to strip the resist off the signal core. MC was used as a control.

Debonding Experiments

The Riston T168, which is a commercial dry film photoresist manufactured by DuPont, was obtained as 60-μm thick film and crosslinked by UV radiation in an atmosphere free of oxygen. The resist is a polymethylmethacrylate (PMMA) based resist. The resist was bonded to thin copper foil. Samples of this bilayer film approximately 1 × 1 cm were clamped over the bottom 0.5 cm to a tall strip of thin metal shim stock (with the Cu side facing the

Table I   *(Continued)*

Solvent (vol %)	Solubility Parameter δ	Hydrogen Bonding	Dipole Moment μ	Solubility Class
41. Dioxane/DMSO (50/50)	11.7	5.4	2.2	S
42. Nitroethane/nitromethane (50/50)	11.9	3.1	3.5	S
43. Acetonitrile	11.9	4.5	3.9	I
44. DMF	12.1	6.4	3.8	S
45. Nitromethane/acetonitrile (60/40)	12.4	3.7	3.6	S
46. Ethanol/DMF (50/50)	12.4	7.7	2.8	I
47. Ethanol/DMF (70/30)	12.6	8.2	2.3	I
48. Nitromethane	12.7	3.1	3.4	S
49. Ethanol	12.8	8.9	1.7	I
50. Ethanol/DMSO (28/78)	12.9	6.1	3.4	I
51. DMSO	13.0	5.0	4.0	I
52. Methanol/DMF (46/54)	13.2	7.6	2.8	I
53. PCO₃	13.3	5.0	4.0	I
54. DMF/monomethylformamide (70/30)	13.3	7.0	3.8	I
55. Methanol/DMF (67/33)	13.7	8.1	2.4	I
56. Methanol/DMSO (57/43)	13.9	7.8	2.7	I
57. Methanol	14.5	8.9	1.7	I
58. PPG	15.0	9.4	2.2	I

S, soluble; I, insoluble. The solubility classification was determined as soluble if the solvent appeared to have dissolved the material to at least the same extent as methylene chloride, and insoluble if less. Concentration of T168 = 13% w/w at 23 ± 2°C.

shim stock) and then placed in a beaker filled with sufficient solvent that the polymer was completely immersed. The geometry of the experimental setup is shown in Figure 1. As the polymer swells the bilayer film bent into a curve with the center of the curvature toward the side opposite the polymer surface causing the shim stock to deflect. The deflection of the shim stock was measured using a Fotonic sensor from MTI-1000 Mechanical Technology Inc. The

probe of this device consisted of two sets of optical fibers that were displaced with respect to one another. One set transmits light to the shim stock and the other collects the light reflected from it. If the end of the probe was initially held farther from the reflecting surface than the spacing between the sending and receiving fiber bundles, a displacement of the reflecting surface (shim stock) away from the probe caused a decrease in received intensity. This intensity was measured by a photocell whose output
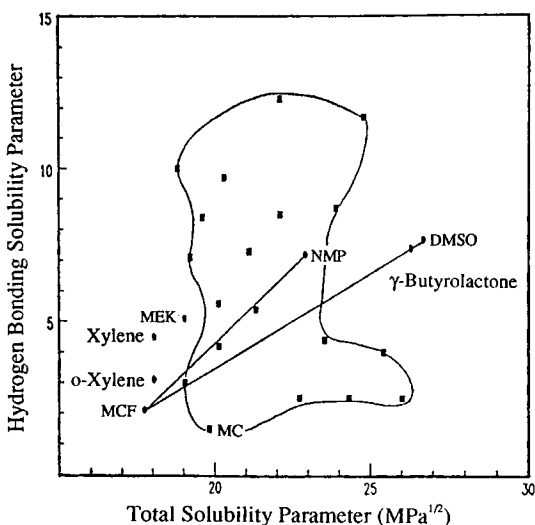

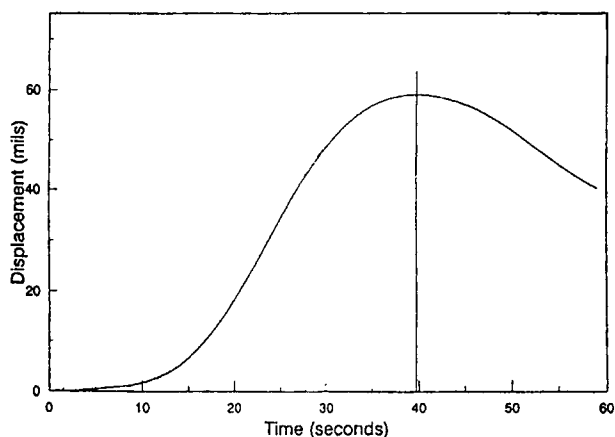**Figure 2**   Solubility of crosslinked Riston T168.

Figure 3   Typical debonding curves of Riston T168 for methylene chloride, 2.2 mil T168, 65 mJ/cm², hold time > 12 h.
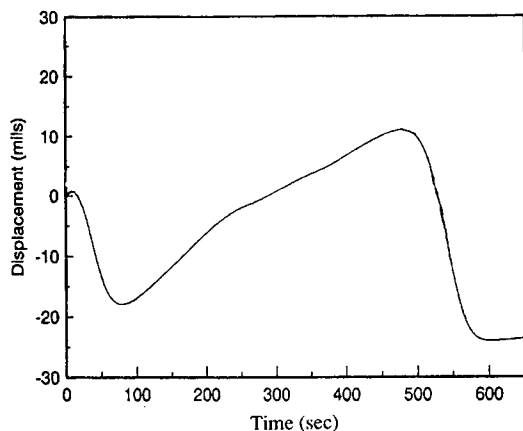
Figure 4 Debonding curves for T168 using propylene carbonate, 2.2 mil T168, 65 mJ/cm², hold time > 12 h.

provided a signal that was a measure of the deflection. Other fiber optics designs could be used. The Fotonic sensor was interfaced to an IBM PC AT computer, to acquire and manipulate the input signal. The apparatus was enclosed in a sealed container that allowed the temperature to be controlled to ±2°C.

A 12 × 12 in. optical isolation table and beam system (Newport Corporation, Fountain Valley, CA) was employed to minimize noise due to vibration. The table was designed to dampen a wide spectrum of vibrational frequencies and also provided a firm base for carrying out the experiment. The beam system insured that the sample holder and the probe tip moved along the same track. The solvent cup was designed to be elevated to the sample via a jack in order to avoid agitation of the solvent.

The solvents tested here were purchased from Aldrich except as otherwise stated: MC as a control, MCF (both Burdick & Jackson) and polypropylene glycol (PPG) redistilled, methyl ethyl ketone (MEK), xylenes, γ-butyrolactone (BLO), n-methyl-pyrollidinone (NMP), and dimethyl-sulfoxide (DMSO). Propylene carbonate (PCO₃), a colorless to amber colored liquid having a high boiling point, high flash point, and low toxicity, was obtained from ARCO under the trade name Arconate® HP.

RESULTS AND DISCUSSION

In our attempts to find potential substitutes to MCF and MC for circuit board manufacturing processes a number of other technologies were investigated. These approaches included acid pattern plating, al-

ternative resist, permanent resist, and alternate nonhalogenated and environmentally benign solvents. Most of these approaches required either extensive developmental efforts or, in the case of an alternative resist, a solvent that was compatible with the electroless copper plating and strippable in aqueous acidic media was not available in the market. Permanent dielectric photoresists were deemed to necessitate lengthy qualification cycles and, hence, were not considered. Alternative environmentally safe solvents was thus the area of our focus.

At this point, it is important to discuss some of the factors governing the solubility of materials in general, and especially the solubility of polymeric systems. Solution thermodynamics dictate that a substance will behave as a solvent for a particular solute when the free energy of solution is negative. The factors that contribute to the free energy of solution are temperature, enthalpy, and entropy and are related by the following equation.

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

The entropy of solution for an amorphous polymer is usually small but positive. This suggests that only a small, positive value for the enthalpy of solution can be tolerated if the free energy of solution for the process is to be negative. Solution must ultimately depend upon the sign and magnitude of ΔH. The enthalpy of mixing for two liquids exhibiting no volume change upon mixing is given by the Scatchard–Hilderbrand equation

$$\frac{\Delta H^m}{V\phi_1\phi_2} = \left[\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right]^2 \tag{2}$$
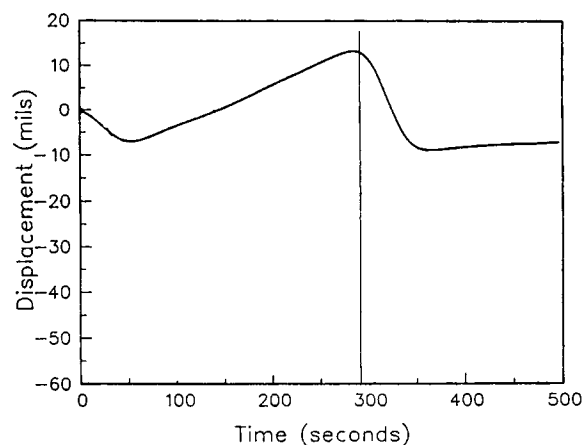

Figure 5 Debonding curves for T168 using propylene carbonate containing 7.8% water, 2.2 mil T168, 65 mJ/cm², hold time > 12 h.

Table II Debonding Time (min) of Crosslinked Riston T168 for Various Solvents

°C	MC	MEK	MCF Fisher	MCF 348 PPG	BLO	DMSO	NMP	PCO$_3$
24	1.5	21	80	190	150	190	190	190
40		4.3	40	45	22	35	17	75
50		1.0	10	15	6	15	8	25
60		0.7	1.8	6	3	5	2.5	8

where ΔH^m is the overall heat of mixing per mole, V is the total volume of the mixture, ΔE_1^v and ΔE_2^v are energies of vaporization of components 1 and 2, V_1 and V_2 their molar volume, and ϕ_1 and ϕ_2 their volume fractions. The most significant term of eq. (2) is $\Delta E^v/V$. This term is the energy of vaporization per unit volume. Because the energy of vaporization at constant volume is the cohesive energy, this term is simply defined as the cohesive energy density. It is obvious from eq. (2) that as the values of the square root of the cohesive energies of the components 1 and 2 approach each other, ΔH^m approaches zero and a negative term for the ΔF of eq. (1) is most likely. This suggests that the probability that two substances will be soluble increases as the difference in their cohesive energy densities decreases. The term $(E^v/V)^{1/2}$ has been redefined as the solubility parameter and has been designated by the symbol δ. Cohesive density is the basis of the original definition by Hilderbrand and Scott of what is now generally called the Hilderbrand solubility parameter or Hilderbrand parameter. This parameter was intended only for nonpolar, nonassociating systems, but the concept has been extended to all systems. The solubility parameter for the solvents may be calculated from the molar heat of vaporiza-

tion and the density of the solvents. These quantities are available from handbooks.[3,4] The molar volume and molar enthalpy information is only available for some liquids, but for the majority of them including all polymers, solids, and surfaces, it is necessary to use indirect methods for evaluating the cohesion parameters.

On the other hand solubility parameters for macromolecules cannot be calculated from their energies of vaporization because they decompose long before their boiling point. An alternate method is available for computing the solubility parameter based on the fact that the cohesive energy density should be an additive property for molecules. Because the δp value is not expected to vary significantly with molecular weight, δp may be estimated by adding the contribution of the individual chemical groups constituting the base unit of the polymer. The most accurate method for the experimental determination of δ is by measuring the volume increase of a lightly crosslinked polymer that has been permitted to swell to
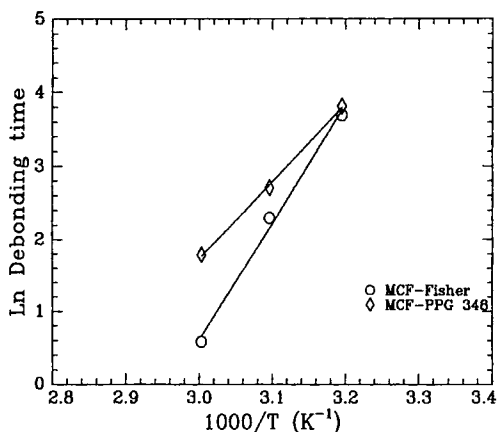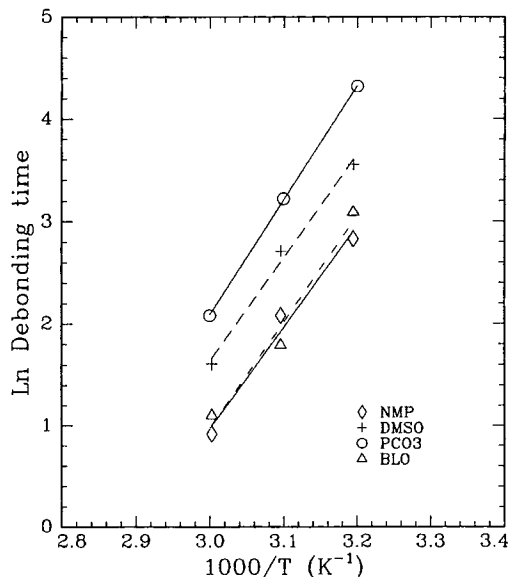

Figure 6 Effect of temperature on the debonding time using MCF as the solvent.

Figure 7 Ln t_b versus $1/T$ for various debonding solvents.

Table III Enthalpy of Activation for Riston T168 Debonding

Solvent	ΔH^* (eV)
PCO_3	1.16
NMP	1.03
BLO	1.08
DMSO	1.05
MC (Fisher)	1.67
MC (PPG 348)	1.09

its equilibrium volume in a solvent of known δ_s. Methods based on the viscosity and turbidity measurements were also used.

Crowley et al.[5] used, in addition to the solubility parameter, the dipole moment together with the hydrogen-bonding parameter. In this way it is possible to produce two-dimensional contour maps to represent solubility behavior for various solvents. Such maps can be used as a means of assisting in a solvent selection.

In our case the solubility parameter determinations were made according to ASTM method D3132. The solubility was determined at 23 ± 2°C in 58 different solvent or solvent mixtures tested according to the Hilderbrand solubility parameter (δ) and hydrogen-bonding index (γ_c). Table I presents all the solvents or mixtures of them used in determining the solubility parameters of Riston T168. The solubility classification was determined as soluble if the solvent appeared to have dissolved Riston T168 to at least the same degree as MC and insoluble if less.

Figure 2 illustrates the hydrogen-bonding solubility parameter versus the total solubility parameter for a number of solvents. The majority of these solvents inside the envelope, although they show activity towards Riston T168, have been noted to be highly toxic and flammable. The lines in the plot indicate that blending of the two nonsolvents could indeed result in a mixture that should fall inside the envelope and exhibit some activity toward Riston T168. Solvents having comparable total solubility parameter and H-bonding index, but are outside the envelope, were considered for evaluation.

The following solvents were tested: MC as a control, MCF and PPG redistilled, MEK, xylenes, BLO, NMP, PCO_3, and DMSO. Mixtures of MEK/MCF and MC/MCF were also tested. The stripping efficiency of these solvents was evaluated according to

the procedure described in the Experimental section using the Fotonic Sensor device.

Figure 3 schematically shows a deflection versus time curve from the debonding experiment when exposing Riston T168 film to MC. As long as the swollen layer remains in contact with its Cu backing, the bilayer sample continues to curl, leading to an increasing deflection as a function of time. As the polymer swells the bilayer film bent into a curve with the center of the curvature toward the side opposite the polymer surface, causing the shim stock to deflect. This intensity was measured by a photocell whose output provided a signal that was a measure of the deflection. When debonding begins, however, the deflection reaches a maximum and rapidly falls to zero as the elastically bent Cu foil returns to its unstressed shape. A convenient measure of the debonding time is the time to the maximum deflection, t_d, as shown in Figure 3. Figure 4 shows typical deflection curves for Riston T168 when PCO_3 is added as the penetrant solvent. Figure 5 represents the results of PCO_3 containing 7.8 wt % water. It is observed that the debonding time is considerably reduced to 300 s versus the 500 s when pure PCO_3 is used. A dramatic decrease in the debonding time as a function of exposure energy was observed and will be the subject of future reports. In fact the unexposed photoresist was shown to be highly soluble in PCO_3.

Table II presents the stripping efficiency results obtained for these solvents. MC used as the control has a a debonding time of 1.5 min at room temperature. At room temperature these solvents do not exhibit any activity, whereas at higher temperatures the debonding times approach those of MC. This may be explained in terms of a faster rate of solvent
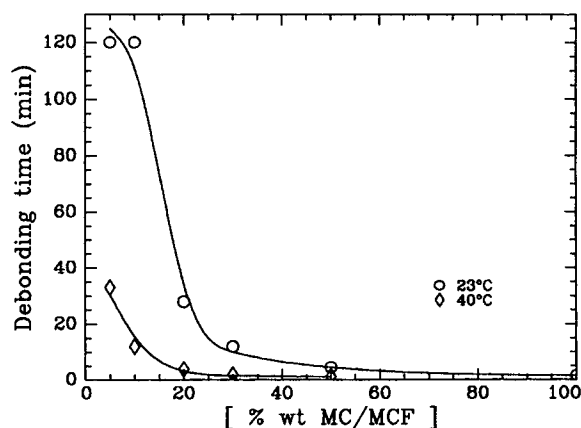
Figure 8 Debonding time as a function of MC/MCF composition.

diffusion to the interface of T168 and epoxy laminate and disrupting this interface resulting in the resist flaking off. Plasticization of the film may be another factor because the glass transition temperature was observed to be in the range of 50°C. It is interesting to note that to obtain comparable debonding time for the other solvents, it is essential that the temperature be raised to higher than 60°C. It was observed that the debonding time is thermally activated with its temperature dependence given by the following equation

$$t_d = Ae^{(\Delta H^*/k_b T)} \qquad (3)$$

where k_b is Boltzmann's constant and A is an empirical constant. A plot of the logarithm t_d versus $1/T$ shown in Figures 6 and 7 results in a series of straight lines that can be used for predicting the debonding time at various temperatures. The activation enthalpy ΔH^* derived from the slopes of the lines in Figures 5–7 are presented in Table III.

There is a distinct difference in the debonding time when MCF is used as the penetrant solvent. The MCF that was used in this investigation was PPG redistilled 348 MCF. The Fisher brand that was used at early stages of the investigations contains stabilizers that enhance the stripping activity. The PPG 348 MCF is free of these components and exhibits slower stripping activity toward Riston T168. These stabilizers were found to consist of the following chemicals: nitromethane, 1, 3 dioxolane, 1, 2 epoxy butane, toluene, isobutanol, and MEK.[6] When these additives were progressively extracted with distilled water, the debonding time increased dramatically.

It appears that the shorter debonding time of the polymer resist on exposure to the unextracted MCF is due to the presence of the small molecule additives. In fact the debonding time should decrease further if small molecules are deliberately added to the unextracted MCF as demonstrated by Mills and Kramer.[6] The debonding time decreases rapidly when small amounts of methanol are added, somewhat less rapidly when iodoethane is added, and only marginally when iodobutane is added. The effectiveness of an additive in decreasing the debonding time of the Riston T168 on exposure to MCF seems to correlate with the debonding time of the film in pure additive, which itself correlates well with molecular size. Mills and Kramer,[6] employing Rutherford backscattering spectrometry, demonstrated that additives that have a molecular volume much less than MCF produce faster debonding of the photoresist and

are particularly effective in decreasing the debonding time of the photoresist as additives to the MCF. These results have been explained in terms of case II diffusion. It is well known that the front velocity in the case II diffusion increases rapidly as the size of the penetrant decreases. The additives that are larger than MCF have case II front velocities in the photoresist that are lower than that of MCF, have longer debonding times, and are relatively ineffective in decreasing the debonding time. The same trend is observed if MCF is blended with MC shown by the debonding times in Figure 8. Once 20 wt % of MC in MCF is reached, the debonding time decreases dramatically, reaching comparable values to pure MC at approximately 40°C. Similar results are observed when PCO_3 contains water. To further understand the underlying mechanism when PCO_3 is used as a penetrant, Rutherford backscattering studies are currently in progress using deuterated PCO_3.

As described in the Introduction, in our efforts to find substitutes to MCF and MC for circuit board manufacturing processes, other technologies such as acid pattern plating and the use of alternative or permanent photoresists were investigated. However, these approaches were found to be cost and time prohibitive for further consideration. Consequently the area of alternate nonhalogenated and environmentally safe solvents remained our focus. Of critical importance, however, is that the commercial utilization of such solvents in photoresist stripping and developing for printed circuit boards greatly depends on a number of specific manufacturing and environmental requirements that include solvent flammability, toxicity, ability to recycle, simplicity of composition, and compatibility with a spectrum of resists.

The stripping efficiency of the solvents identified as environmentally safe (Table II) can be compared with the solvency power of MC at various temperatures. At room temperature these solvents show negligible if any activity toward the photoresist. At processing temperatures of 60°C, even though the solvent stripping efficiency improves, the debonding times are 2–5 times lower than that of MC observed at room temperature. These experimental findings correspond to the debonding times of BLO and PCO_3, respectively. The debonding time decreases at higher temperatures than 60°C, reaching comparable response to MC. Accordingly, either solvent fulfilling the manufacturing and environmental requirements previously addressed could be adopted in the fabrication of circuit boards. NMP may also be an option; however, its strong swelling

properties and subsequent potential detrimental effect to the base epoxy laminate make it less attractive for use.

CONCLUSIONS

In summary this work identifies a number of non-toxic and safe solvents for stripping and developing Riston T168 efficiently. Results of this study indicate that the stripping efficiency of these solvents approaches that of MC only if the temperature is maintained higher than 60°C. Based on these findings, the low toxicity, low volatility, commercial availability, and nondetrimental effect on the base laminate of either PCO_3 or BLO make them possible substitutes to MCF and MC.

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