Laminate Materials for No-Lead Solder Applications

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Introduction

Environmental concerns about lead entering ground water systems has led to legislation to ban the use of lead in many applications including water pipes and paint. Over the past ten years, attention has been focused on smaller applications, which include the lead-containing solders used in the electronics industry.

Traditionally, electronic-grade solder has a composition of about 63% tin (Sn) and 37% lead (Pb). The Pb component of this solder reduces the melting point (Sn m.p.= 232 ^oC) of the solder to 183 ^oC and substantially increases the wettability of liquid solder, and increases the strength of solder joints.

There has been extensive research on lead substitutes. Candidate materials include various combinations of Sn, Cu (Copper), Ag (Silver), Al (Aluminum), Zn (Zinc), Bi (Bismuth) and In (Indium). Solders made with Bi and In have significantly lower melting points than the current leaded variety. However, negligible worldwide supplies and high costs will probably preclude serious consideration of these metals as lead replacements.

Solders using alloys of Sn with Cu, Ag and sometimes Al all have significantly higher melting points than the incumbent. Some examples are listed in Table 1[1].

Table 1 – Examples: Solder Alloys and Their Melting Points

Alloy	Melting Point (^oC)
63Sn – 37Pb	183
100Sn	232
Sn – 4Cu – 0.5 Ag	216
Sn – 3.5Ag	221
Sn – 9Zn	199

The apparent front runner for general soldering, specified by the National Electronic Manufacturers Initiative (NEMI) is the Sn-Cu-Ag alloy[2]. There are variations of this alloy using slightly different amounts of Cu and Ag, with slightly different melting points. With a melting point around 216 ^oC , reflow temperatures near 250 ^oC or higher are likely.[2] Some original equipment manufacturers (OEMs) are already specifying higher thermal performance requirements, such as a T-288 test (time to delamination at 288 ^oC) or multiple solder float exposures at temperatures in excess of 550 ^oF. This increase in temperature will stress the thermal performance of most current PCB resin systems.

The current trend in the PCB industry is towards thicker boards requiring smaller coefficients of thermal expansion (CTE). To achieve this lower CTE and minimize costs, FR-4 resin systems with a T_g in the 170 ^oC range are currently used. However, current systems have T-260 times in the neighborhood of five to ten minutes. Testing at 288^oC, as requested by some OEMs, results in times-to-delamination of essentially zero minutes.

This paper will discuss the development of new resin systems that will withstand the higher reflow temperatures required of lead-free solders, while meeting the expectations of PCB manufacturers concerned with both the ease of fabrication processing and providing cost competitive solutions in today's global marketplace.

Background / Discussion

FR-4 has historically used dicyandiamide (Dicy) as a curative chemistry. These epoxy resins has been relatively stable, easy to process and available at a reasonable cost. However, the cross-linked network obtained with this system degrades readily at higher temperatures. The 170^oC T_g systems are more susceptible than lower T_g systems to thermal degradation because some thermal stability was sacrificed in order to make these materials process like the lower T_g systems they replaced.

In order to increase the thermal performance of the resin system while maintaining processability and cost requirements, a new resin system will be required. It is quite likely that such a system will incorporate a different curing agent. The chemical discussion of epoxy curing systems is outside the scope of this paper, but references are cited at the end of the paper for the curious reader.

Requirements for a New Substrate

Through review of industry assessments and working with several OEMs and PCB fabricators, it became clear that a new epoxy/E-glass substrate was required. Today's formulator has an ever increasing number of commercial raw materials from which to select in order to meet the performance criteria for next generation copper-clad laminate products suitable for lead-free solder applications. Therefore, development activities were focused on the laminate performance evaluation of base epoxy resins, resin modifiers and curing systems that are expected to meet PCB processing, productivity and cost requirements, in addition to the enhanced thermal property targets listed in Table 2. The trend toward increased layer counts and reduced feature sizes in thicker circuit board designs is challenging PCB requirements. In particular, next generation resin systems will be expected to yield high quality, thermally resistant plated-through-hole (PTH) innerconnects with higher aspect ratios. New circuit board designs are including mechanically drilled PTH vias as small as 8 to 10 mils (0.008 to 0.010 inch.). Additionally, PCB lamination times will need to be reduced in order to achieve increasing productivity targets.

Results

Numerous test laminates were produced in the laboratory for thermal performance evaluation. Resins systems studied were formulated in solvent and used to impregnate standard 7628 style E-glass cloth to ~45% retained resin. Prepregs were B-staged to the desired resin flow in a forced-air convection oven set at 170°C then heat-laminated using ½ oz. reverse-treat copper foil cladding. Laminates were cured under pressure (200 PSI) for 35 minutes at a cure temperature of 170°C, without additional post baking. Test laminates were then screened for physical properties performance using standard industry test methods. Two resin systems meeting the targeted design criteria were then selected for subsequent laminate and PCB prototype evaluations. The resultant laminate properties are compared to typical property values for the current 170°C epoxy product offerings in Table 3. In each case, the new products demonstrate measurably improved thermal properties. This data predicts increased PCB thermal resistance and reliability.

As a result of the preliminary screening trials on laminates, PCBs were fabricated on both of these systems at different PCB manufacturers. Several board designs, ranging from standard test boards to 16-layer, 0.093-inch boards incorporating 0.010-inch drilled holes were built. These boards, along with standard 170°C epoxy boards, were fabricated with standard, conventional processes. However, the cure system used in both new materials is faster than the traditional Dicy curing agent and reductions in lamination cycles of 30 minutes or more are possible. These laminate cycle reductions will be studied at a later date. There were no observed issues with manufacturing circuit boards on these materials. Standard drills and drilling parameters were utilized. Micrographs of magnified (200X) 0.0135-inch hole walls obtained form condition. A micro-sections are compared in Figure 1. Smoother PTHs can be achieved with the new products.

Table 2 – Comparison: Thermal Properties of Current and Next Generation Substrates

Property	Units	Typical Values Epoxy 170°C	Target Values Next Generation
Tg by DSC	°C	170	170-180
T-260 Resistance by TMA	Min	10	45-60
T-288 Resistance by TMA	Min	<1	15-30
CTE (Z-axis below Tg by TMA)	ppm/°C	65	55-65
Solder Float Resistance @ 288°C	Sec	100-200	300-400
Td by TGA (onset)	°C	290	320-350

Table 3 – Comparison: Laminate Properties of Current and New Substrates

Property	Units	Typical Values 170°C Epoxy	Next Generation Product A	Next Generation Product B
Tg by DSC	°C	170	175	180
T-260 Resistance by TMA	Min	10	45	60
T-288 Resistance by TMA	Min	<1	15	25
CTE (Z-axis below Tg by TMA)	ppm/°C	65	65	65
Solder Float Resistance @ 288°C	Sec	100-200	500	600
Decomposition Temp. by TGA (onset)	°C	290	325	340
Peel Strength (1/2oz. Reverse-treat)	Pli	6.5	6.0	5.0
Comparative Tracking Index (CTI)	Volts	175	200	175
UL 94 Flammability		V-0	V-0	V-0

The thermal properties of the PCBs were also characterized. These data are listed in Table 4. Again, the thermal resistance benefits of the new products were observed. Although some of the T-260 times are low, the mode of failure location was at the oxide interface, explaining the lower board thermal performance than the base laminate's. The thermal integrity of the PTHs was then tested by exposing the PCB coupons to six thermal shock cycles. For each cycle, the coupons were floated on a solder bath at 288°C for 10 seconds and then allowed to cool to room temperature before repeating. Micrographs obtained from subsequent microsectioning analyses are depicted in Figure 2. As predicted, the improved thermal resistance of the two new products was demonstrated in improved hole reliability.

Conclusions and Future Research

New resin formulations are being developed that will meet the thermal requirements of the new, lead-free solders. These systems have better thermal properties, drill better and potentially will cure faster.

Research is currently underway to study oxide processing and alternatives to maintain adhesion of resin to copper under high temperatures and thermal stress conditions. Lamination cycles are being optimized, as are drilling parameters, to improve both productivity and quality.

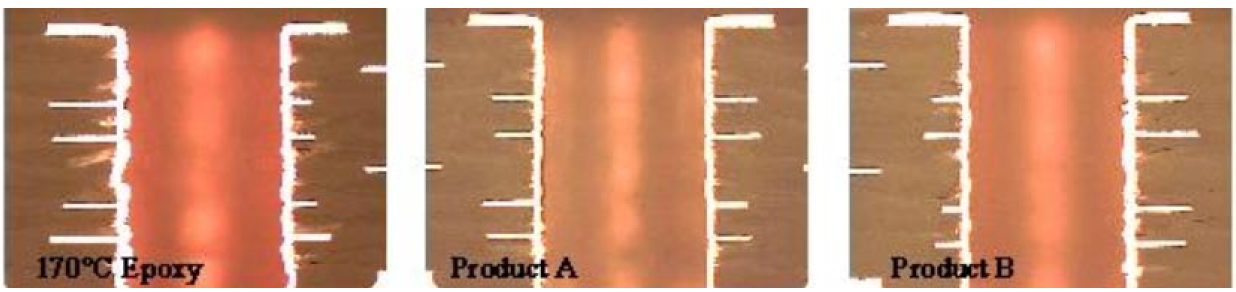

Figure 1 – Comparison: 0.0135" PTH Quality of Current and New Substrates

Table 4 – Comparison: PCB Properties of Current and New Substrates

Property	Units	Typical Values 170°C Epoxy	Next Generation Product A	Next Generation Product B
Tg by DSC	°C	173	176	183
Tg by DMA	°C	180	180	192
T-260 Resistance by TMA	min	2.6	7.0	6.6
CTE (Z-axis by TMA, 20-260°C)	ppm/°C	178	176	161
Decomposition Temp. by TGA (onset)	°C	290	325	331
Moisture, As Received	%	0.10	0.12	0.11

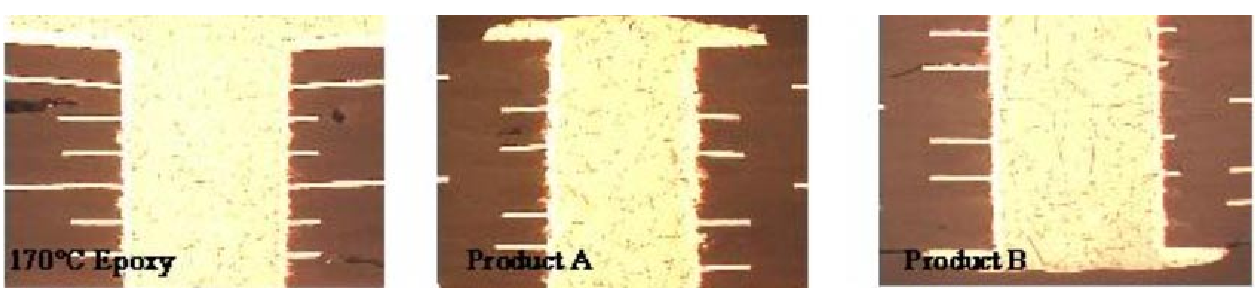

Figure 2 – Comparison: 0.0135" PTH's Exposed to 6 x 10 sec. Thermal Shock at 288°C

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