IMPROVED PRODUCT RELIABILITY THROUGH
THE CONTROL OF MOISTURE

By F. L. Gentry and J. W. Lula

BDX-613-2291

Distribution Category
UC-38

Manuscript submitted:

IPC Fall Meeting

Institute for Interconnecting and Packaging Electronic Circuits
September 26, 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States, nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

The Bendix Corporation
Kansas City Division
P. O. Box 1159
Kansas City, Missouri 64141

A prime contractor with the United States
Department of Energy under Contract Number
DE-AC04-76-DP00613

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

alternative, thermal mechanical analysis (TMA) was developed as a means to quantitatively measure the delamination resistance of multilayer PWBs.

Multilayer PWBs are tested at Bendix on standard TMA laboratory equipment using an expansion probe (Figure 2). The test specimen is prepared by punching a 0.25-inch-diameter disc from a multilayer PWB using a sheet metal hand punch (Figure 3). To minimize distortion of the specimen, the punch has been modified to flatten the face. After placing the test specimen in the fixture (Figure 4) and lowering the expansion probe with a 10-gram tray weight, the equipment is programmed for a 20°C/minute temperature rise from room temperature to 260°C, which represents molten solder, at which point the temperature is held constant. A recording chart moving at a constant rate simultaneously records the temperature and expansion of the test specimen. Helium is flowed through the fixture during the test to control heat conductivity and to purge the fixture of outgassing products.

A typical TMA chart for a six-conducting-layer multilayer PWB is shown in Figure 5. Point A, the point at which the expansion curve changes slope, is the glass transition temperature (T_g) of the laminate. Point B, the point at which the expansion curve levels off, corresponds to the temperature leveling off at 260°C. The sharp spike at point C is the blistering of the test specimen.

The time interval between point B and point C is the t_{260} of the laminate and is a measure of the delamination resistance.

The TMA's sensitivity to changes in the processing of multilayer PWBs has been verified. Examples of the effects that the processing variables have on the TMA results are shown in Figures 6, 8, and 9, which are the TMA curves of three different laminates. To maintain full copper to prepreg interface, no circuitry was etched on the panels. Only the interlayer surface treatment and prepreg conditioning were varied in the processing of the test panels. All were cured at 182°C and 300 PSI for 60 minutes.

Figure 6 shows the TMA curve of a test panel which had no interlayer surface treatment other than a hand scrub with a pumice cleaner followed by a thorough DI water rinse. The prepreg, which had been refrigerated, was brought up to room temperature and then removed from its package and layed up immediately. As the TMA curve of this laminate shows, the T_g is 124°C. The t_{260} is not measurable because a blister occurred at 244°C, which was 1.2 minutes before the temperature reached 260°C. As an additional test, peel tests were performed on one-inch-wide strips which were sheared from the laminate. When an outer copper-clad layer was peeled at 90° from the remaining portion of the laminate at the copper/prepreg interface, the result was 0.7 pounds per inch width. Production multilayer PWBs made to this process will

delaminate during solder dipping, solder leveling, or drag soldering. Delaminations also will occur during quality checks as the boards are cross-sectioned and mounted for plated through hole analysis (Figure 7).

Figure 8 shows the first improvement made. The copper-clad panels were treated with a commercial black oxide process. The prepreg was conditioned identical to the previous laminate. As can be seen, the T_g remained unchanged. However, the t_{260} is 2.5 minutes, indicating the laminate is much more resistant to delaminations at soldering temperatures. Peel strength was tested as before, and only a slight improvement to 0.9 pounds per inch width was noted. Production multilayer PWBs made with black oxide will survive solder dipping, solder leveling, and drag soldering without delamination. The ability to withstand soldering processes is directly related to the t_{260} as shown in Figure 8. When cross-sectioned for plated through hole analysis, however, delaminations which are related to the low peel strength can occur.

Figure 9 shows the greatest improvement. In this case, in addition to the black oxide interlayer surface treatment, the prepreg was held in a vacuum for 24 hours to remove moisture. The prepreg was then removed from the vacuum chamber and immediately layed up into a laminate. The T_g has risen considerably, up to 137°C .

The t_{260} has almost doubled, increasing to 4.5 minutes. The most remarkable improvement was in the peel strength: it increased by more than 10 times to above 10 pounds per inch width. Some samples were as high as 25 pounds per inch width. Multilayers made with this process have no delamination problems, either in soldering processes or in cross-sectioning during quality analysis.

Prepreg Conditioning

At this point in the project, it seemed obvious the presence of moisture within GF prepreg resulted in decreased delamination resistance between the copper circuitry and the cured prepreg layers. This was detected by TMA and showed up as lower T_g and t_{260} values. The presence of moisture was also observed in the resin squeeze-out of the cured laminates (Figure 10). In the absence of moisture, the squeeze-out is clear and the flow is reduced. As the moisture content increases, bubbles appear in the squeeze-out and the flow increases. This can be quantified by measuring the specific gravity and percent flow of the resin squeeze-out.

Because the initial work with the TMA revealed the degrading effect that moisture has on multilayer PWBs, subsequent work focused on prepreg conditioning. Prepreg conditioning concerns the removal of moisture from epoxy/glass prepreg prior to lamination and cure of a multilayer PWB. Because GF prepreg may contain

up to 0.75% volatiles (mostly moisture) as allowed by MIL-G-55636, these must be removed to obtain acceptable delamination resistance. Our prepreg, as received from the vendor, is averaging 0.35% volatiles. During this project, we have determined the requirements for controlling moisture in GF prepreg which involves removing the moisture, maintaining the prepreg in a dried state, and preventing an excessive reabsorption of moisture upon exposure to a 50% relative humidity environment.

Three methods were evaluated to remove moisture from prepreg:

1. Container storage with a desiccant;
2. Vacuum treatment; and
3. Dry nitrogen storage.

Of these, container storage with a desiccant is the slowest and least acceptable. For all practical purposes, vacuum treatment and storage in dry nitrogen will remove absorbed moisture at an equal rate. Storage in dry nitrogen is preferred because it is more cost effective to implement in a manufacturing process.

The rate of moisture removal by vacuum from GF prepreg has been determined by laminating 8-inch by 10-inch six-conducting-layer

laminates as shown in Figure 11. The prepreg, all from the same manufacturer and lot, was vacuum treated (less than 5 mm Hg pressure) for various lengths of time. The copper clad panels were oxide coated and baked for 1 hour at 120°C prior to lamination. Panels were then removed from the oven and immediately layed up. The laminates were cured at 182°C for 1 hour under 300 PSI. Following the cure, the resin squeeze-out was broken off and weighed. The percent flow was calculated by dividing this weight by the original weight of the uncured prepreg. In addition, the average specific gravity of the resin squeeze-out was measured and TMA tests were performed on the laminate. The results are given in Table 1.

From a delamination resistance standpoint (t_{260}), not much improvement is seen after 60 minutes of vacuum treatment. There is still moisture present, as indicated by the continued changes in the specific gravity. Prepreg should be conditioned either by vacuum treatment or dry nitrogen storage for a minimum of 24 hours to ensure complete removal of moisture. Under manufacturing conditions, 48 hours is preferred to maintain a satisfactory margin.

Once the moisture has been removed, the prepreg must be maintained in a dried condition. It has been the practice in the past to refrigerate GF prepreg until use; therefore, a test was run to

determine the degradation of prepreg at room temperature while stored in dry nitrogen. A quantity of unconditioned prepreg, from the same manufacturer and lot, was removed from refrigeration and placed in a dry nitrogen storage cabinet. At set periods of time, six conditioned sheets were used to make a laminate similar to that described previously. The copper-clad panels were oxide treated and baked for 1 hour at 120°C prior to lamination. The laminate was cured at 182°C for 1 hour under 300 PSI. Upon removal from the lamination press, the flow and specific gravity of the resin squeeze-out were measured, and TMA tests were performed on the laminate (Table 2).

From the TMA results, it appears that an acceptable laminate is still being made after 6 months of dry nitrogen storage. The T_g of the laminate remains at a high level, and the t_{260} is still above 3 minutes. The specific gravity remains generally constant, which verifies the absence of moisture in the prepreg. Based on this data, and keeping in mind the high degree of quality consistency normally required of multilayer PWBs, a maximum dry nitrogen storage time of 28 days is recommended. This point is chosen because the flow begins to noticeably decrease after this time.

The Bendix manufacturing department in which prepreg is used has a relative humidity of $45 \pm 15\%$. After removal from the dry nitrogen cabinet, moisture immediately begins to absorb into the

prepreg. A test was run to determine the rate at which this occurs and how this affects the multilayer PWB. Laminates were made as before using GF prepreg which had been stored in dry nitrogen for 24 hours then allowed to hang in 50% RH/room temperature air for varying lengths of time. The prepreg was then layed-up with oxide-coated copper-clad panels and cured for 1 hour at 182°C under 300 PSI pressure. Tests were performed as before, and the results are given in Table 3.

The data in Table 3 shows that moisture reabsorption is rapid and that this definitely needs to be considered when laminating multilayer PWBs. To maintain part-to-part consistency, a maximum of 5 minutes is recommended between removal of the prepreg from the nitrogen cabinet and the start of the laminating press cycle.

Moisture and Cured Multilayer PWBs

The absence of moisture has been shown to be important during the lamination process. In addition, moisture also influences cured multilayers. Even though moisture may be controlled during lamination, the multilayer immediately begins to absorb moisture from the environment as soon as the unwanted copper on the outer surface is etched off. The rate of absorption depends upon the moisture concentration in the environment. The time it takes for a multilayer to reach equilibrium with the moisture in the air

depends upon the thickness of the board. Figures 12 and 13 illustrate these points. Unless they are stored in a dry condition, multilayer PWBs will be of lower quality and more prone to failure at the soldering operations, which is the harshest test the board will see throughout its life. Controlled packaging is being implemented to assure that a dry condition is maintained.

The effect moisture has on a multilayer PWB has been investigated through the use of TMA. Several TMA test specimens were punched out of a laminated test panel identical to those used for all previous testing. A quantity of test specimens was placed in 10, 30, 50, and 100% RH chambers. At set time intervals, a specimen was removed from each chamber and tested on the TMA. The t_{260} was calculated and plotted and the results are shown in Figure 14. Any storage condition with a relative humidity over 10% (at room temperature) caused a measurable degradation of the test specimens. We did try to recover the properties by baking the remaining samples, but were not entirely successful. Subsequently, it appears preferable to maintain multilayer PWBs at a dry condition rather than bake out prior to soldering operations. This is currently being investigated.

An additional effect of moisture on cured laminate is that of expansion in the X-Y plane. Test specimens 0.5 by 5.5 inch by 0.018 inch were stored in various humidities and measured at

various set intervals of time. The results are given in Table 4. No other work has been done on this subject, but the information is given here to increase awareness about internal stresses resulting from moisture absorption.

Bendix has used the information gained from this project to improve the lamination quality of their multilayer PWBs. The predominant change has been the implementation of dry nitrogen storage cabinets to condition prepreg prior to lamination (Figure 15). To aid in drying, the prepreg is hung by fanning out on the racks rather than stacking (Figure 16). In addition, once the prepreg is removed from the cabinet, it is used immediately and multilayer lay-ups are no longer being made in advance, waiting for the press.

Another change made is in the multilayer panels. An area has been added which enables a TMA sample to be taken if desired for lot-to-lot monitoring (Figure 17). This was done during the first phase of the project to observe the quality improvement.

Through this study, we at Bendix have become much more aware of the problems associated with moisture and have taken steps to control it in the manufacture of multilayer PWBs. As a result, delaminated multilayer PWBs are no longer a problem at Bendix.

Figure 1. Delaminated Multilayer
Printed Wiring Board

Figure 2. Thermal Mechanical Analysis Equipment

Figure 3. Panel, Test Specimen, and Hand Punch

Figure 4. Close-Up of Specimen in Fixture

Figure 5. Typical TMA Curve of an Acceptable Six-Layer PWB

Figure 6. TMA Curve for Multilayer PWB: No Innerlayer Surface Treatment; No Prepreg Conditioning

Figure 7. Delamination From Cross-Sectioning

Figure 8. TMA Curve for Multilayer PWB: Black Oxide Surface Treatment; No Prepreg Conditioning

Figure 9. TMA Curve for Multilayer PWB: Black Oxide Surface Treatment; Moisture Removed From Prepreg

Figure 10. Resin Squeeze-Out

Figure 11. Laminate Assembly

Table 1. Vacuum Treatment (<5 mm Hg Pressure)
of GF Prepreg

VACUUM TREATMENT TIME (MINUTES)	RESIN SQUEEZE-OUT		t_{260} DELAMINATION RESISTANCE (MINUTES)
	FLOW (PERCENT)	SPECIFIC GRAVITY	
NONE	28	0.75	1.2
15	26	1.10	2.1
60	25	1.19	3.8
120	24	1.26	4.0
240	22	1.27	4.0
24 HOURS	22	1.37	4.1

Table 2. Dry Nitrogen Storage of GF Prepreg

TIME (DAYS)	RESIN SQUEEZE-OUT		LAMINATE	
	FLOW (PERCENT)	SPECIFIC GRAVITY	T _g (°C)	t_{260} (MINUTES)
NONE	28	0.75	133	1.2
2	20	1.35	134	4.4
7	19	1.36	137	5.0
14	19	1.30	137	4.7
21	19	1.26	135	4.4
28	20	1.25	133	4.3
60	17	1.29	132	4.3
91	14	1.32	132	4.9
181	11	1.30	132	3.4
365	8	1.30	123	3.0

Table 3. Moisture Reabsorption in GF Prepreg

TEST DESCRIPTION*	RESIN SQUEEZE-OUT		t_{260} DELAMINATION RESISTANCE (MINUTES)
	FLOW (PERCENT)	SPECIFIC GRAVITY	
NO ADDITIONAL MINUTES	25	1.33	3.6
5 MINUTES	27	1.31	4.1
15 MINUTES	27	1.20	3.1
60 MINUTES	29	0.86	1.9
24 HOURS	31	0.75	0

*LAMINATES WERE CONDITIONED FOR 24 HOURS IN N_2 PLUS INDICATED ADDITIONAL TIME IN 24°C, 50 PERCENT RH.

Figure 12. Percent Moisture Absorption Versus Time for Different Thickness

Figure 13. Percent Moisture Absorption Versus Time for Different Humidities

Figure 14. t_{260} Versus Storage Time in Relative Humidity of Improved Laminate PWB (0.034-Inch-Thick GF Epoxy/Glass)

Table 4. Hygroexpansion Coefficient Determination of Stabilized FR-4 Epoxy/Glass PWB Material

HUMIDITY	INITIAL LENGTH (IN.)	7 DAYS	14 DAYS	30 DAYS	90 DAYS	48 HOURS AT 250°F	MOISTURE CONTENT (%)	HYGROEXPANSION COEFFICIENT (IN/IN % R.H.)
10%	5.5042	5.5041	5.5038	5.5040	5.5042	5.5034	0.11	0
30%	5.5036	5.5049	5.5047	5.5046	5.5046	5.5034	0.25	6.8×10^{-6}
50%	5.5051	5.5056	5.5068	5.5067	5.5069	5.5048	0.42	6.6×10^{-6}
100%	5.5030	5.5083	5.5089	5.5093	5.5098	5.5033	1.00	11.6×10^{-6}

NOTE: ABOVE FIGURES ARE AVERAGES OF THREE SAMPLES

Figure 15. Dry Nitrogen Storage

Figure 16. Prepreg Hanging Fixture

Figure 17. Panel Showing TMA Area