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Improving Delamination Resistance of Multilayer Printed Wiring Boards

By J. W. Lula

MASTER

Published March 1980

Topical Report

Prepared for the United States Department of Energy
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Bendix Kansas City Division

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Technical Communications Bendix Kansas City Division

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Copper oxide innerlayer surface treatment and prepreg moisture content influence the delamination resistance of multilayer printed wiring boards made from flame-retardant epoxy-glass. Surface treatment roughens and passivates the copper circuitry enhancing the bond strength at the copper and prepreg surface interface. With a copper oxide innerlayer surface treatment and the moisture removed from the prepreg, multilayer printed wiring boards made from epoxy-glass material will withstand from 2 to 6 minutes immersion in molten solder without delamination.

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CONTENTS

ILLUSTRATIONS

TABLES

SUMMARY

Multilayer printed wiring boards (PWB) made from the National Electrical Manufacturers' Association (NEMA) FR-4 material (flame-retardant epoxy-glass) must have the copper circuitry surfaces converted to an oxide (innerlayer surface treatment) and the moisture removed from the prepreg (prepreg conditioning) in order to consistently withstand production soldering processes without delamination.

Innerlayer surface treatment roughens and passivates the copper circuitry surfaces. Roughening the surface increases the mechanical bonding of the copper to prepreg, while passivating the surface prevents undesirable chemical reactions from taking place at the epoxy-copper interface during cure. The oxide formed by innerlayer surface treatment may be either a black oxide (cupric oxide) or a red oxide (cuprous oxide). Both of these oxides are obtained by immersing cleaned innerlayer panels in caustic solutions containing a strong oxidizing agent such as sodium chlorite, at an elevated temperature for a specified length of time. For practical purposes, both black and red oxides can provide acceptable delamination resistance for a multilayer PWB. Adhesion obtained using red oxide is less dependent on processing variables such as time of immersion and temperature of the oxidizing solution. However, thermomechanical analysis (TMA) test specimens made with red oxide are easily separated following the TMA test. Those specimens made with black oxide still maintain their integrity in spite of the TMA test. For this reason, black oxide is recommended over red oxide for use in multilayer PWBs.

Prepreg conditioning of FR-4 material prior to lamination is required to remove the moisture (up to 0.75 percent) normally present in the prepreg as it is received from the vendor. The mechanism by which moisture is detrimental to the copper-prepreg adhesion is not completely understood but the results are clear. When used in combination with oxide treatment of innerlayers, removal of moisture prior to lamination of a multilayer PWB will increase the interlaminate adhesion by more than 10 times and double the length of time the multilayer PWB can be immersed in molten solder without delaminating. Three means for removing moisture from prepreg have been investigated: desiccation, vacuum treatment, and storage in dry nitrogen. Of these, storage in dry nitrogen is the most practical to use in production areas because of its simplicity. The FR-4 prepreg should be conditioned for at least 24 hours and preferably 48 hours prior to lamination. The prepreg may be stored in dry nitrogen for 4 weeks without noticeable decrease in the quality of the finished laminate.

FR-4 prepreg, which has been stored in dry nitrogen, rapidly regains moisture upon exposure to the humidity in the air. In a 50 percent relative humidity, 24°C laboratory environment, 5 minutes is recommended as the maximum time allowed between removal of prepreg from dry nitrogen and the start of the lamination press cycle.

DISCUSSION

SCOPE AND PURPOSE

This project was undertaken to develop a lamination process which will consistently produce ultrathin multilayer printed wiring boards free from delamination problems. During this phase of the project, various methods for increasing the delamination resistance have been evaluated. The effect on the delamination resistance as well as the adaptability to current production processes have been considered.

PRIOR WORK

An effective test method for measuring the delamination resistance of multilayer printed wiring boards (PWB) has been developed. This method uses thermomechanical analysis (TMA) and provides a quantitative measurement of the delamination resistance at soldering temperatures. TMA also provides the glass transition (Tg) temperature of the laminate which not only is an indication of the degree of cure but also is a function of the moisture content in the cured laminate. During the development of this test method, innerlayer surface treatment and prepreg conditioning were found to have the greatest effect on interlaminate adhesion.

ACTIVITY

This project began as a result of an excessive number of delamination rejects occurring on ultrathin multilayer PWBs manufactured at Bendix. The delaminations were at the copper/prepreg interfaces and occurred during solder dipping, solder leveling, and drag soldering. Delaminations also occurred when boards were sectioned during quality control analysis for plated-through-hole evaluation. During the first phase of this project it was discovered that innerlayer surface treatment and prepreg conditioning were critical areas to be considered when laminating multilayer PWBs. These are the areas discussed within this report.

Innerlayer Surface Treatment

Delaminations of multilayer PWBs were occurring because the bare copper-epoxy prepreg bond lacked the strength to survive high-temperature processes such as solder dipping, solder leveling, and drag soldering. Innerlayer surface treatments roughen and passivate the copper circuitry surfaces. The roughening provides a stronger mechanical bond while the passivation prevents the following detrimental reaction from taking place.

$$R - \underset{OH}{CH} - R' \xrightarrow[200^\circ C - 300^\circ C]{Cu} R - CH - R' + H_2$$

When the reaction does take place, hydrogen gas can be a factor in delamination when the multilayer PWB is subjected to high-temperature processes. Researchers investigating this reaction have measured 100 to 1000 ppm of hydrogen per 645 mm^2 when epoxy multilayer PWBs were heated to 175°C in a sealed container.[1]

Innerlayer surface treatments for multilayer PWBs refer to converting the copper circuitry surfaces to a copper oxide. Three copper oxide innerlayer surface treatments have been tested during this project; two treatments convert the copper to a black oxide (cupric oxide, CuO), and one treatment converts the copper to a red oxide (cuprous oxide, Cu_2O). Proprietary commercial products were used for producing the black oxides, and a solution prepared in the laboratory was used to produce the red oxide.

The oxide treatments were applied, as specified in the Appendix, to 1/1 copper-clad NEMA FR-4 laminate having 0.127 mm core thickness. The proprietary oxide solutions were prepared according to manufacturers' recommendations, and the red oxide solution was prepared according to Table 1. Oxide thickness varied with respect to the temperature of the oxide solution and the immersion time. The copper clad panels were 203 by 254 mm and no circuitry was etched on them. Following the oxide treatment, they were baked at 120°C for 1 hour to remove adsorbed moisture; then, they were laminated into a five-layer multilayer PWB using FR-4 prepreg (108 style glass fabric) which had been stored in dry nitrogen for 24 hours. After that, the layup (Figure 1) was cured at 182°C for 60 minutes at 2.1 MPa with no postcure.

Following cure, samples of these laminates were tested by TMA using a procedure outlined in a previous report.[2] TMA testing of a multilayer PWB will give the degree of cure indicated by the Tg and also a quantitative measurement of the delamination resistance at soldering temperatures (t_{260}). This latter number may be visualized as the length of time in minutes the laminate will remain in molten solder at 260°C without delaminating. The TMA results for the two black oxide treatments are given in Figure 2.

Actually, any thickness of black oxide tested provides a multilayer PWB with adequate delamination resistance with respect that no delaminations would be expected to occur during normal processing as long as moisture-free prepreg was used. However, with

Table 1. Composition of Red Oxide Solution

Chemical Name	Symbol	Amount (g/L)
Sodium Chlorite	$NaClO_2$	30
Sodium Hydroxide	NaOH	10
Trisodium Phosphate	Na_3PO_4	5
DI Water*		

*Deionized

both black oxides there appears to be an optimum time-temperature window. Either a too-thick or too-thin black oxide coating results in reduced delamination resistance.

Manufacturers' literature indicates that black oxide coatings will withstand temperatures up to 205°C. At higher temperatures, the bond between the copper oxide coating and the base copper is slowly destroyed. As a result, red oxide treatment has been recommended for high-temperature laminates such as polyimides because of the red oxides' greater stability compared with black oxide at the higher cure temperatures. Some laminate manufacturers have also proposed its use for standard epoxy-glass laminates. Therefore, it was decided to evaluate red oxide in addition to black oxide. The solution for converting copper to red oxide was prepared as outlined in Table 1. Copper clad FR-4 panels were coated, laminated, and tested (Figure 1).

With red oxide, as with black oxide, any of the time-temperature processing conditions tested would result in acceptable delamination resistance, as long as moisture-free prepreg was also used. Red oxide does maintain optimum results over a wide range of time-temperature conditions, an advantage over black oxide. A concern, though, is that the TMA specimens easily separate after the test. This separation does not happen with black oxide specimens, which remain intact following the TMA test. Thus, in spite of claims to the contrary, the red oxide solution tried is not suitable for high-temperature laminate work.

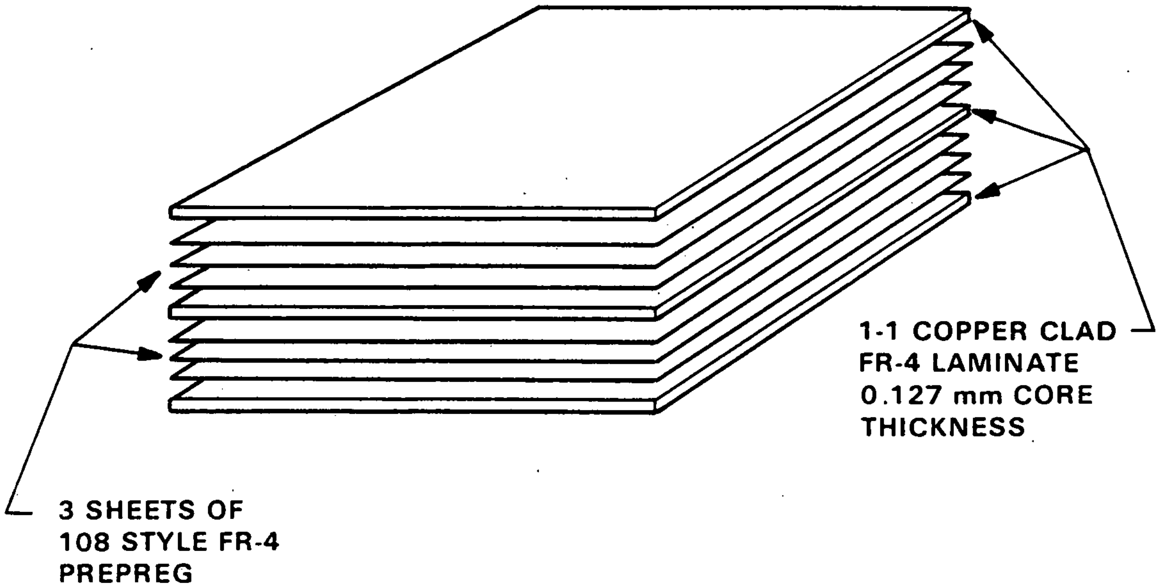

Figure 1. Construction of Five-Layer Multilayer PWB

Prepreg Conditioning

Prepreg conditioning concerns the removal of moisture from epoxy-glass prepreg before lamination and cure of a multilayer PWB. Because FR-4 prepreg may contain up to 0.75 percent volatiles (mostly moisture), as allowed by MIL-G-55636, these must be removed to obtain acceptable delamination resistance. It is a misconception to believe that the resin flow during lamination removes moisture. It is true that moisture is carried out with the resin flow, but an equal concentration of moisture remains within the laminate. This project has determined the parameters for controlling moisture in FR-4 prepreg in a dried state and reabsorption of moisture upon exposure to a 50 percent relative humidity environment.

The presence of moisture within FR-4 prepreg will result in decreased delamination resistance between the copper circuitry and the cured prepreg layers. This resistance can be detected by TMA and shows up as lower Tg and t_{260} values. Also, moisture can be observed in the resin squeeze-out of the cured laminate. 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 reaction can be quantified by measuring the specific gravity and percent flow of the resin squeeze-out.

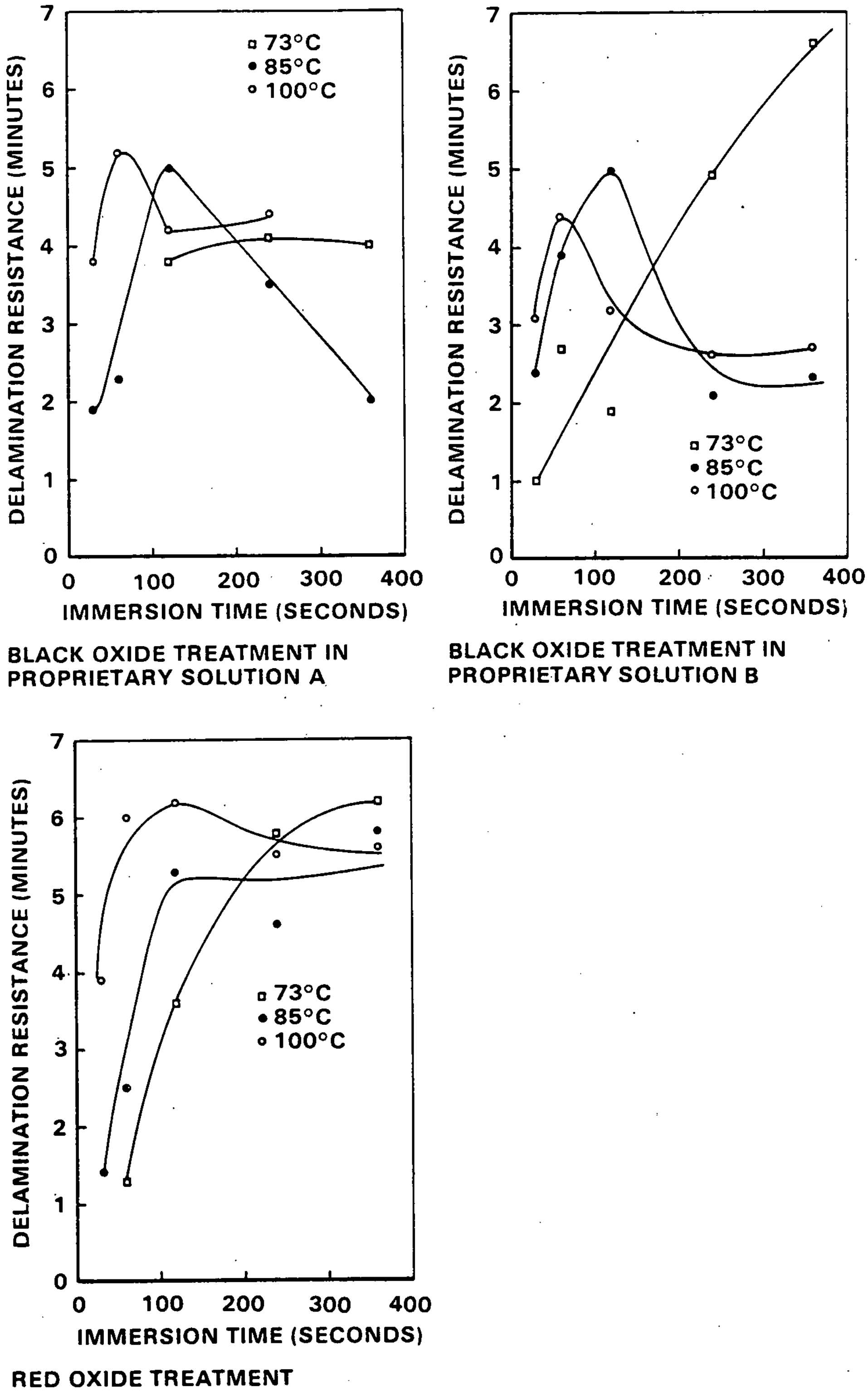

Figure 2. Resistance to Delamination Following Solution Treatment

Three methods were used to remove moisture from prepreg:

Container storage with a desiccant,

Vacuum treatment, and

Storage in a cabinet continually purged with dry nitrogen.

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 the simplest to implement in a manufacturing process.

The rate of moisture removal from FR-4 prepreg has been determined by laminating five-layer, 203- by 250-mm laminates as shown in Figure 1. The prepreg used was vacuum treated for various lengths of time. The copper clad panels were oxide treated and baked for 1 hour at 120°C prior to lamination. The laminates were cured at 182°C for 1 hour under 2.1 MPa with no postcure. 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 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 in Table 2.

The results in Table 3 show the effects of removing moisture from FR-4 prepreg. From a delamination resistance standpoint (t_{260}), not much improvement is seen after 60 minutes of vacuum treatment. There is still moisture present though, as indicated by the continued increase 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 as a result of these tests in order to maintain a satisfactory margin for error.

Once the moisture has been removed, the prepreg must be maintained in a dry condition. Since it has been the practice in the past to refrigerate FR-4 prepreg until use, a test was run which determined the degradation of prepreg at room temperature while stored in dry nitrogen. A sufficient quantity of prepreg was removed from refrigeration and placed in a dry nitrogen storage cabinet. Periodically, six sheets were removed and used to laminate a five-layer, 203- by 254-mm multilayer (Figure 2). 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 2.1 Mpa with no postcure. Once cured, the flow and specific gravity of the resin squeeze-out were measured, and TMA tests were performed on the laminate (Table 3).

Table 2. Vacuum Treatment of FR-4 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 3. Dry Nitrogen Storage of FR-4 Prepreg

	Resin Squeeze-Out		Laminate	
Time In (Days)	Flow (Percent)	Specific Gravity	Tg (°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

From the TMA results, it is apparent that an acceptable laminate is still being made after 6 months of dry nitrogen storage. The Tg 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 these data, and keeping in mind the high degree of quality and 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 manufacturing department in which prepreg is used has a relative humidity of 50 percent. Immediately after removal from the dry nitrogen cabinet, moisture 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. Five-layer laminates were made as before (Figure 2) using FR-4 prepreg which had been stored in dry nitrogen for 24 hours then allowed to hang in the laboratory air (50 percent RH) 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 2.1 Mpa, with no postcure. Tests were performed as before, with the results in Table 4.

The data in Table 4 show 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.

ACCOMPLISHMENTS

During this phase of the project, Bendix has incorporated black oxide innerlayer surface treatment and dry nitrogen prepreg conditioning into the manufacturing process for multilayer PWBs. Before these changes, interlaminar adhesion was marginal and delaminations regularly occurred during solder dipping and leveling. Since the implementation of these changes, Bendix has not experienced any delaminated multilayer PWBs, and they may be immersed in molten solder for 2 minutes or more without visual damage.

Both black oxide and red oxide innerlayer surface treatments have shown the capability to provide acceptable delamination resistance for multilayer PWBs made from FR-4 material. Optimum processing parameters for applying the oxide treatment have been determined.

In order to manufacture a multilayer PWB that will withstand solder dipping/leveling as well as subsequent drag soldering, it is necessary to remove absorbed moisture from the prepreg before lamination. Data have been gathered on the rate of moisture removal from prepreg when dried and on the rate of moisture reabsorption when dried prepreg is exposed to 24°C/50 percent RH environment.

Table 4. Reversibility of Dry Nitrogen Storage

Test Description*	Resin Squeeze-Out: Flow (Percent)	Resin Squeeze-Out: Specific Gravity	t_{260} Delamination Resistance (Minutes)
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 kept for 24 hours in N_2 plus indicated additional time in 24°C, 50 percent RH.

FUTURE WORK

The next and final phase of this project will involve testing laminates made from different cure cycles. The effort will be directed toward optimizing the Bendix process with respect to time, pressure, temperature, and cool-down requirements. The final goal will be cost improvement and higher productivity while maintaining the current high level and lamination quality.

REFERENCES

[1]P. Schuessler, "Preventing Delamination of Circuit Boards and Flexible Circuits," Insulation Circuits, Volume 19, Number 8, July 1973, pp 34-35.

[2]J. W. Lula, Testing the Interlaminate Adhesion of Multilayer Printed Wiring Boards (Topical Report). Bendix Kansas City: BDX-613-2011, September 1978 (Available From NTIS).

Appendix

COPPER OXIDE INNERLAYER SURFACE TREATMENT

1. Pumice hand scrub
2. Tap water rinse
3. 60 second immersion in ammonium persulfate solution (180 grams/liter)
4. DI water rinse
5. 60 second immersion in 30 to 40 percent hydrochloric acid
6. DI water rinse
7. Immersion in oxide solution for specified time and temperature
8. DI water rinse
9. Isopropyl alcohol rinse
10. Static air dry

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