Impact 2010 – Paper US052 – Revised 11/4/10

Title: The role of moisture in red color formation and delamination, including the Root Cause, Mechanism and Prevention.

Background

We have seen a number of instances where the typical OA (Oxide Alternative) dark brown coating has turned red during lamination, typically with DICY (Dicyandiamide) cured and traditional halogenated FR4 materials.

Typically, when the red color change is observed after lamination, we have also seen reduced Tg and ΔTg >6^0C, poor thermal resistance and cases of premature delamination during component reflow and wave soldering. These observations indicated incomplete cross-linking of the resin system during lamination.
Also, with the same materials, we have seen the red color change following delamination result in material decomposition and premature delamination failure during thermal reliability testing or assembly soldering. In these cases, the color change appeared to be exacerbated by increased reflow temperatures. We suspected a direct connection between the two.

Given the high moisture absorption of many DICY cured materials, there was much speculation, and empirical evidence, indicating trapped moisture was the primary reason for the color change and pre-mature delamination failure. However, we had not been able to conclusively prove the correlation between trapped moisture, change in color and pre-mature delamination.

Case Studies

- Many tests were performed to isolate the root cause of the red color change. Testing included evaluating a number of new and old OA baths, at a wide range of process and chemical conditions, low/high temperature and low/high pressure lamination cycles. But we were unable to re-create the problem during these tests using the above variables. We did see that thicker, darker OA coatings were more likely to show a change to red.
- The problem initially appeared to be specific to DICY cured materials, with “Halogen Free” and most High Tg PN types generally not susceptible. Sometimes the problem was specific to one type of prepreg while other customers had seen a problem with a variety of DICY cured low Tg prepreg materials.
- Typically the red color change appears around the outside edges of the panel, suggesting a concentration of moisture as it was squeezed out to the edges during vacuum lamination (Fig 1). Delamination of red color areas was usually evident after reflow, in the same red color edge areas (Fig 2).

Fig 1 Before Reflow

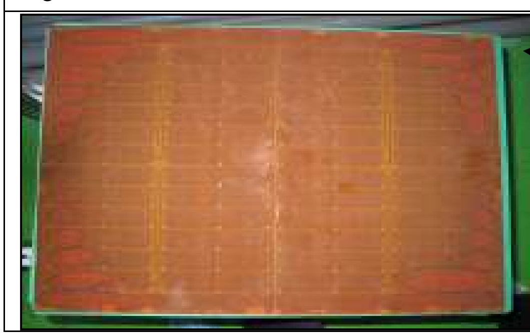
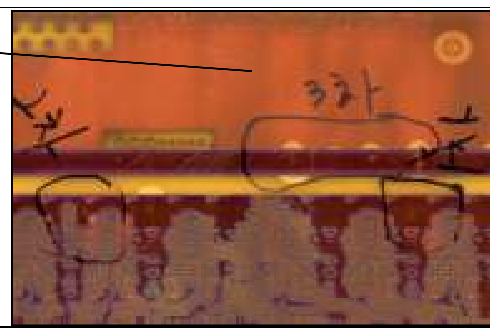


Fig 2 Delamination after Reflow



- Very often the red color change was seen as streaks “flowing” out to the panel’s edges after lamination. The red color streaks appeared to originate from large etched areas, indicating some outgassing from the laminate material (Fig 3).

Fig 3 After lamination (outer layer copper etched away)

Red Color also visible as streaks, from panel center outwards

- We had also seen red color change and premature delamination failure when the vacuum sealed prepreg packages had been left open for extended time before lamination and also with extended hold time between lay-up and lamination, indicating the possibility of moisture absorption as a potential key factor. Some materials appeared to be more susceptible to red color following extended hold time, especially in high humidity environments.

- After comparing the incidence of red color change by individual lamination presses at one customer, we saw that presses with lower vacuum pressure during lamination were more susceptible to the red color change.

Press No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Average Vacuum Pressure (Inches/Hg)	20	27	17	20	18	28	22	26	22
No. of reddening parts (8/22-10/28	6	1	21	5	11	1	2	1	3
Danger Level of red color	High	Low	High	High	High	Low	Mid	Low	Mid

These observations confirmed that press vacuum pressure conditions had a key role in the formation of red color and provided direction for further testing to identify and prove the actual root cause. Red color problem was eliminated following press maintenance to optimize vacuum conditions in all lamination presses.

- SEM/EDS examination of premature delamination failure areas after reflow, indicated higher than normal levels of bromine in those areas (Fig 4 & 5).

Fig 4

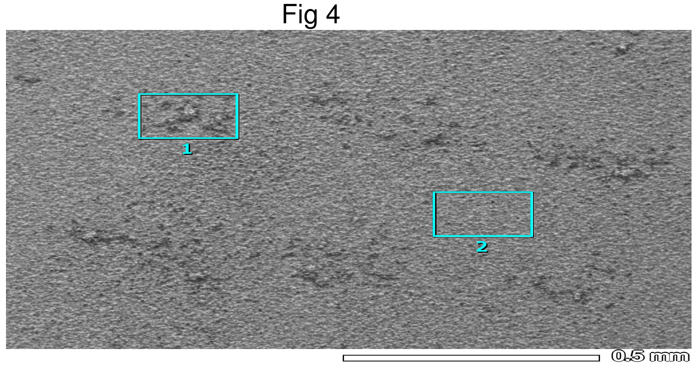
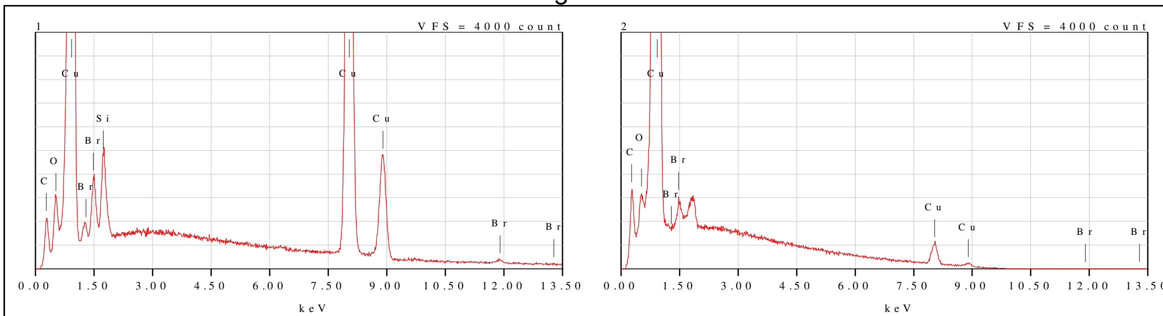


Fig 5

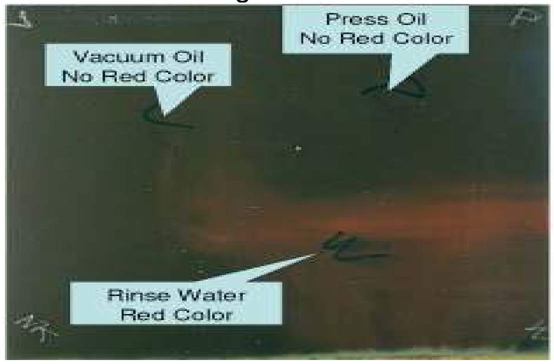


mass%

	C	O	Si	Cu	Br	Total
1	6.75	1.67	1.55	87.13	2.90	100.00
2	6.81	1.58		89.33	2.28	100.00

- An initial indication that trapped moisture was indeed the root cause when prepreg was contaminated with press oil, vacuum oil and rinse water from the press plate scrubber. 2 ml of each were placed on the inner layer core under the prepreg, before lamination. Only the area with rinse water exhibited a red color change (Fig 6).

Fig 6



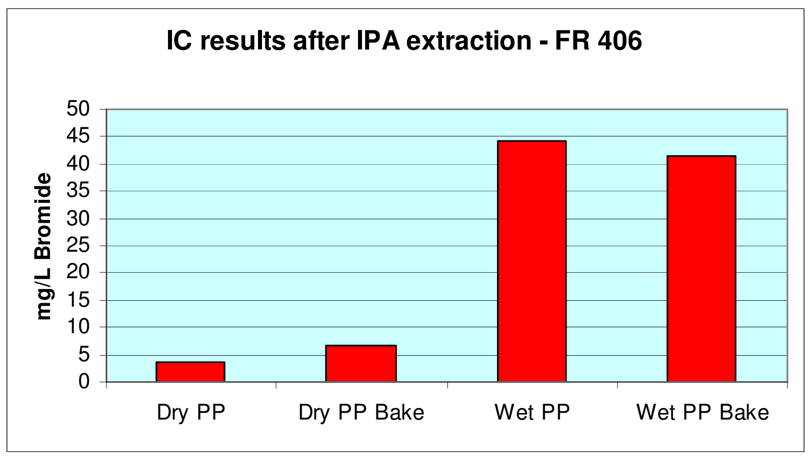
Customer experience and in-house testing concluded that as a group, DICY cured “low to mid Tg” materials, including Isola FR 406, were most susceptible to change color.
With co-operation from Isola, FR 406 was chosen for further testing designed to fully identify the root cause, the mechanism and also to define lamination conditions that can prevent the red color change.

Root Cause

Our testing identified a threshold level of moisture in the prepreg before the color change was evident after lamination. Short term prepreg storage of 24 hours in high humidity conditions did not create the color change. However, extended prepreg storage of 72 hours in high humidity conditions or one drop of water inside the package before lamination resulted in the red color change. We confirmed that “Halogen Free” prepreg materials were not susceptible to the red color change, under the same conditions. We also confirmed that trapped moisture in the prepreg during lamination resulted in reduced thermal reliability and premature delamination during reflow (Fig 7).

Fig 7 - Results after Reflow

Fig 8



Mechanism

Using IPA extraction and Ion Chromatography we identified the mechanism of the red color change as being caused by high levels of Bromides released from “wet” prepreg during lamination. UV/Vis analysis was used to quantify and compare relative levels of bromides in “wet and “dry” prepreg after lamination. The samples were first baked at 200^{0}C for 140 minutes to accelerate any resin decompostion. The results clearly showed a significant increase in Bromide when “wet” prepreg was used. (Fig 8)

We theorized that moisture in the prepreg interferes with the curing mechanism and destabilizes the brominated fire retardant compounds in the DICY prepreg material [1], releasing bromides that combine with the moisture to form corrosive volatiles, reducing the dark brown Cu+2 to a red brown Cu+1, changing the OA coating from a dark brown to a red color.

$$2Br^- + 2Cu^{+2} = 2Cu^{+1} + Br_2\uparrow$$

After delamination, we confirmed by EDS that the same corrosive volatiles were released during decomposition of the prepreg material.

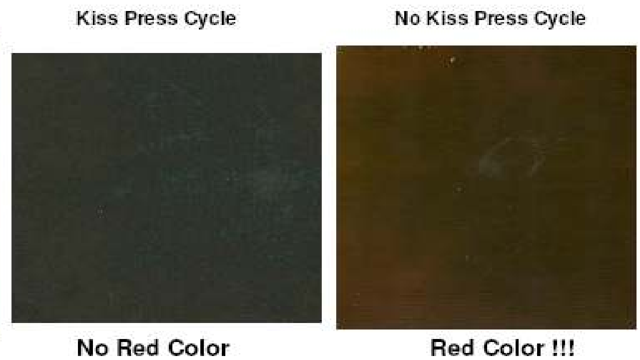
Prevention

Based on our initial work, showing that optimized vacuum pressure in combination with low initial clamping pressure appeared to eliminate the red color formation, we theorized that initial high clamping pressure and low vacuum pressure "seals" the edges of the package before the moisture can be removed.
Accordingly, we evaluated the effect of two different lamination cycles using "wet" and "dry" prepreg.

1. An initial low temperature 30 minutes "kiss" step, with full vacuum pressure before applying clamping pressure was added, to allow for optimized moisture removal,.
2. A standard "no kiss" cycle, with full clamping pressure applied before complete vacuum drawdown.

Results clearly indicated that using a low temperature "vacuum desiccation" or "kiss" step as the first step in the lamination cycle effectively removed moisture from the package and prevented the red color change caused by trapped moisture (Fig 9 & 10).

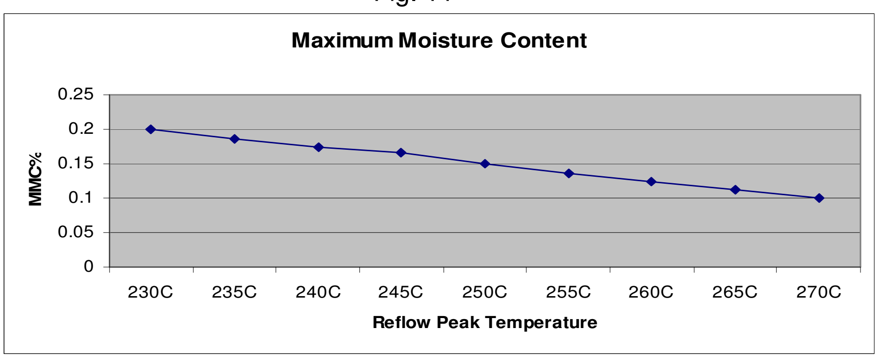
Fig 9 - One Drop of water added before lamination   Fig 10 - 72 hours at 280C and 95% relative humidity



In addition to preventing condensation on the prepreg and low humidity storage conditions of opened prepreg packages is also very important to minimize any hold time of the inner layers in high humidity conditions following inner layer DES.

Subsequent testing has determined that maximum allowable moisture content varies with materials and the intended assembly reflow conditions. Generally 0.1% is considered the maximum for lead–free assembly. Certainly moisture content above 0.2% has shown to cause significant performance and delamination problems (Fig. 11).

Fig. 11



[1] Different Curing Systems Can Improve Laminate Performance. Y.R. Peng, S Zhao, C. Chrisafides. The Board Authority, June 2004.

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