Contamination of Hydrocarbon Ceramic Dielectric

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Abstract
Various forms of contamination on the surface of hydrocarbon ceramic dielectric PWBs have been observed following component population. Although contamination is occasionally observed on PWBs fabricated from other dielectric materials, the light color of hydrocarbon ceramic substrates increases the frequency of detection, and consequently increases the number of investigations into possible contamination causes and impacts to reliability. Three contamination types are evaluated: staining due to rework of gold plated surfaces, discoloration due to flux application, and the resulting anomalies due to the effects of multiple chemical processing steps. The causes of the anomalies, quantitative analysis of residues, and impacts to reliability for each of these contaminants are discussed.

Introduction
High reliability electronics, and especially those in space applications, must often function for years without repair or replacement. Adding to the challenges in hi-rel electronics is the methodology used to perform reliability calculations: PWBs are assumed to be 100% reliable. Therefore, the Class 3 and 3/A requirements in the IPC design, construction, and acceptability (inspection) documents[1-3] are critical pieces of ensuring mission success. The presence of contaminants could possibly introduce several negative impacts to reliability. Contaminants on the surface of PWBs could possibly be conductive and cause electrical shorts. Alternatively, when used in high frequency applications, the contaminants might alter the dielectric constant of the laminate enough to alter performance. Also of concern are electro-migration effects[4,5] such as dendrite growth on the surface of a PWB, or for deep stains, conductive anodic filament (CAF) formation within the dielectric.

In the course of PWB population, several assembled PWBs were discovered that showed the presence of unknown contaminants and stains on their dielectric surfaces. Such stains violate the acceptability criteria contained within IPC-6012[2]. Stains typical of those observed are shown in Figure 1. Through subsequent analysis, the contaminants and discolorations were found to be the result of a number of causes. In one case, it is believed that purple stains were the result of gold plating rework. In another, brown stains resulted from prolonged exposure to RMA flux. In a third example, staining resulted from the processing involved in construction of the multilayer PWB. All PWBs were fabricated from IPC-4103/10[6] hydrocarbon-ceramic dielectric. As this dielectric is white in color, the discolorations were highly visible and resulted in holds being placed on the assemblies following visual inspection. This paper will discuss three types of contamination discovered; the analyses performed to identify the contaminants, and will discuss any reliability impact due to their presence.

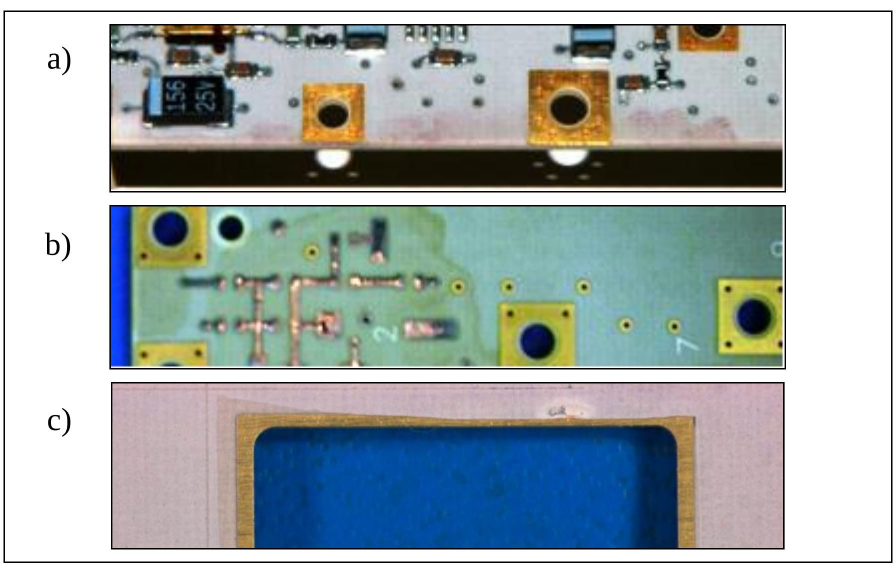

Figure 1 – (a) Purple staining on an assembled printed wiring board's edge. (b) Brown staining on an unassembled PWB. (c) Staining around periphery of cutout in PWB.

Discussion and Analysis

Purple Stains:

The first of the stains discovered were observed on populated multilayer PWBs with plated and fused tin-lead solder pads and gold plated mounting locations, see Figures 1 and 2. The stains were not discovered prior to component population. The lack of detection prior to soldering was puzzling since all PWBs are inspected prior to assembly. To determine the nature of the stain and to try and establish whether the stain posed a reliability risk several tests were performed. The most immediate concern was whether the purple stain was conductive and might cause an electrical short. To evaluate this possibility a sample of the stained laminate was removed with a razor blade and was analyzed by energy dispersive x-ray (EDX) spectroscopy. The EDX spectrum is shown in Figure 3. No metals were found in any concentration that would cause an electrical short. The small amount of iron found is consistent with other non-contaminated samples removed with a steel blade. Additional dielectric withstanding voltage tests of electrodes bridged by stained dielectric showed no detectable leakage current when 500V DC was applied.

One aspect of the purple stained PWBs was that they consistently appeared on boards near gold plated mounting bosses. Due to the proximity of the stains to the gold surfaces, the stains were conjectured to be the result of plating solution residue from the touch-up of gold surfaces.

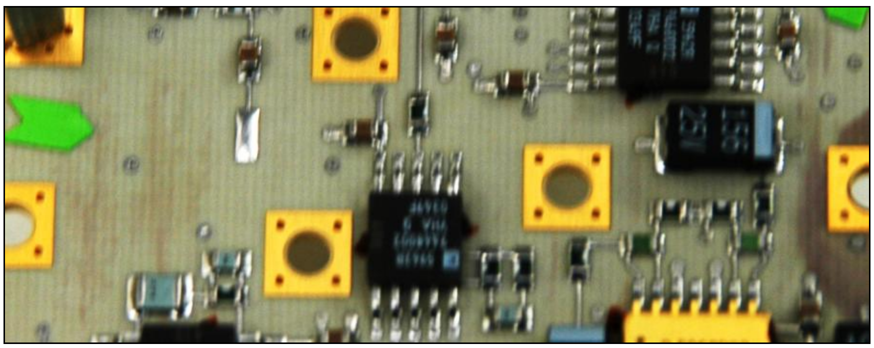

Figure 2 – Purple staining on a populated PWB. The staining is most prominent around the gold plated surfaces.

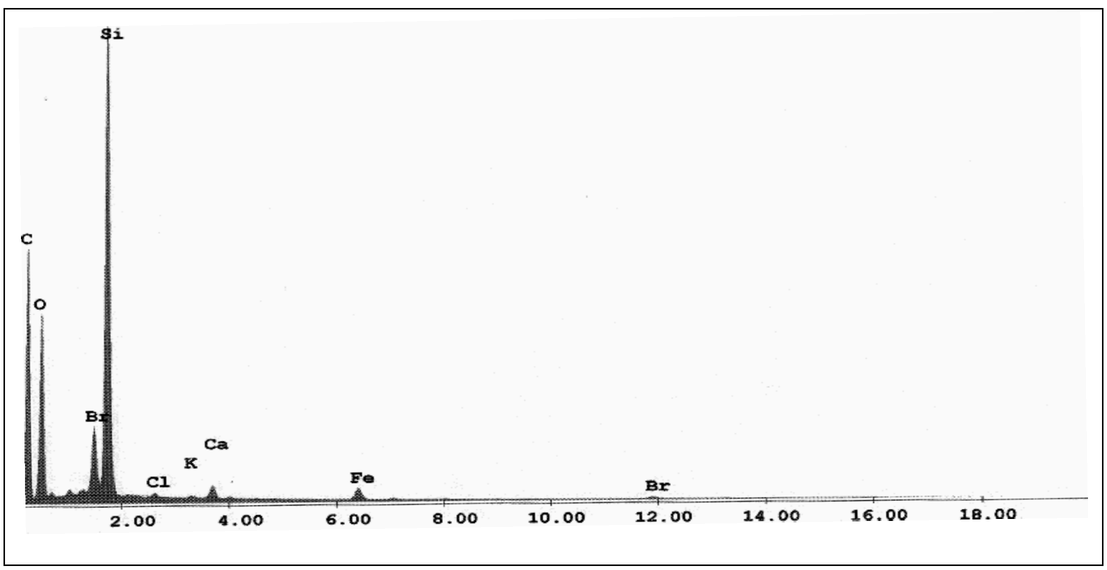

Figure 3 – EDX spectrum of purple stained dielectric.

To verify that the source of the stains was plating solution, several unstained coupons from affected and unaffected PWB lots were exposed to gold plating solution. After prolonged exposure, the coupons did not immediately exhibit the purple stains that affected populated assemblies did. However, after the coupons underwent a soldering simulation in a convection reflow oven, all appeared stained purple. It is believed that the purple color is brought out when stained boards are exposed to heat such as during convection reflow.

Once the origin of the stains was identified, the potential risk of electrochemical migration became the greatest concern. Several studies have demonstrated a link between ionic contaminants on a PWB and the board's susceptibility to dendrite growth[7,8], and to CAF formation[9]. Probing of the anomalous PWBs showed that the laminate was only stained on the surface of the dielectric making CAF formation a low risk. However, dendrites are the product of ionic migration on the surface of a dielectric making the presence of the plating solution stains on the PWB surface a reliability concern. The severity of the ionic contamination was first assessed by Ion Chromatography (IC) and Inductively Coupled - Plasma Mass Spectrometry (ICP-MS).

The analyses were performed by removing 6 cm2 areas from both stained and unstained boards that were then carefully broken into smaller pieces. For IC analysis, the samples were placed separately into pre-cleaned autosample vials to which deionized water was added. The vials were then capped and sonicated. The extracts were quantitatively analyzed for cationic and anionic components by IC. For ICP-MS analysis, the samples were placed separately into vials and digested in aqua-regia (3 parts concentrated hydrochloric acid and 1 part concentrated nitric acid). The resultant digests were diluted with deionized water and introduced to a rhodium internal standard. All samples were compared with various standards in concentrations up to 20 ppb.

The results of the elemental analysis (Table 1) showed that copper, zinc, and aluminum were major components in both the unstained and stained samples. Most of the conductive salts on the stained sample were found to be 2 to 3 times more abundant than on the unstained sample.

Table 1 – ICPMS results of both unstained and stained PWB samples.

Parameter	In Unstained Board Sample ($\mu g/cm^2$)	In Stained Board Sample ($\mu g/cm^2$)
Metals		
Aluminum	**Major**	**Major**
Chromium	0.32	0.47
Iron	1.5	5.1
Nickel	0.41	0.74
Copper	**Major**	**Major**
Zinc	**Major**	**Major**
Tin	0.16	0.39
Antimony	0.26	0.34
Gold	0.42	2.2
Lead	0.17	0.45
Cations		
Lithium	ND < 0.08	ND < 0.08
Sodium	0.39	1.4
Ammonium	ND < 0.08	1.0
Potassium	0.29	0.43
Calcium	ND < 2.5	ND < 2.5
Magnesium	ND < 0.3	ND < 0.3
Anions		
Fluoride	ND < 0.08	ND < 0.08
Chloride	0.45	0.73
Bromide	0.10	0.30
Nitrate	ND < 0.8	ND < 0.8
Phosphate	ND < 3	ND < 3
Sulfate	0.45	5.5

ND = Not detected

Now that it was clear that the stained samples had slightly higher ionic contamination levels, it was necessary to assess the risk posed by dendrite formation. To do this water droplet tests were performed on IPC E coupons from lots of parts similar in construction to the affected assemblies. The test setup is schematically illustrated in Figure 4. An electrical bias was established across two electrodes that were bridged by a deionized water droplet. In the tests performed, the electrode spacing on all E coupons was 20 mils and a voltage bias of 20 V was applied across the electrodes with a 1 MΩ current limiting resistor in series with the power supply. Each test was run for a maximum of 30 seconds per coupon.

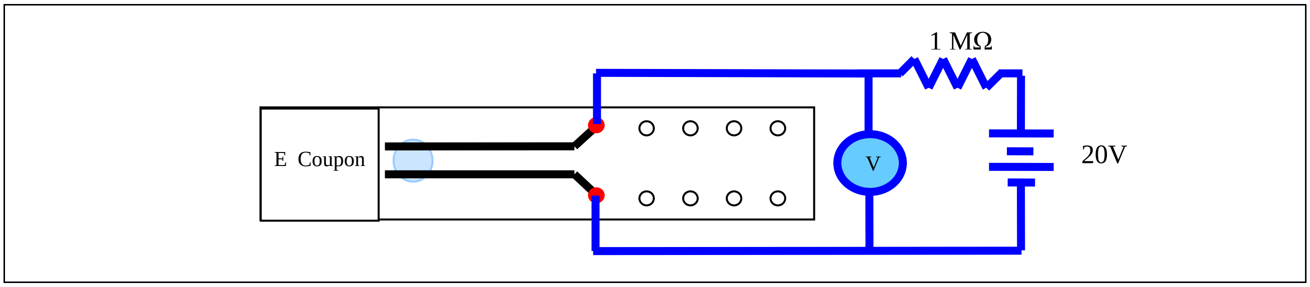

Figure 4 – Water droplet test schematic. Water drop is shown bridging left end of "Y" pattern electrodes.

Although often subjective, stained coupons seemed to grow more dendrites, a longer distance, in a shorter period of time than the unstained control group. However, no differences between the two groups were significant. A typical dendrite formation is shown in Figure 5. Results are plotted in Figures 6 through 8.

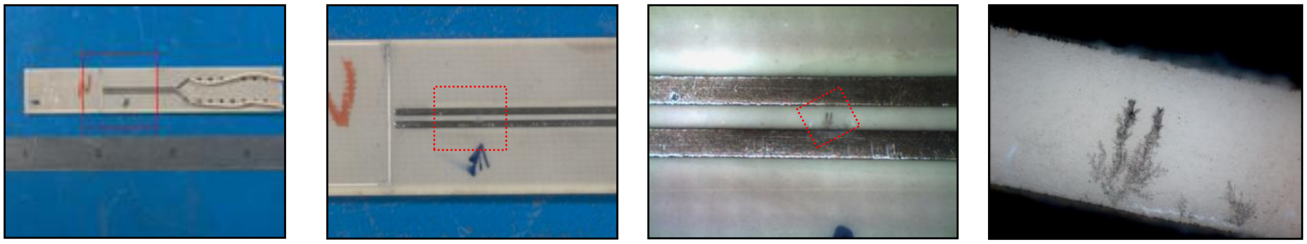

Figure 5 – Photos from a stained E coupon following 30 seconds under a 20V bias. Magnification of photos increases as you move to the right.

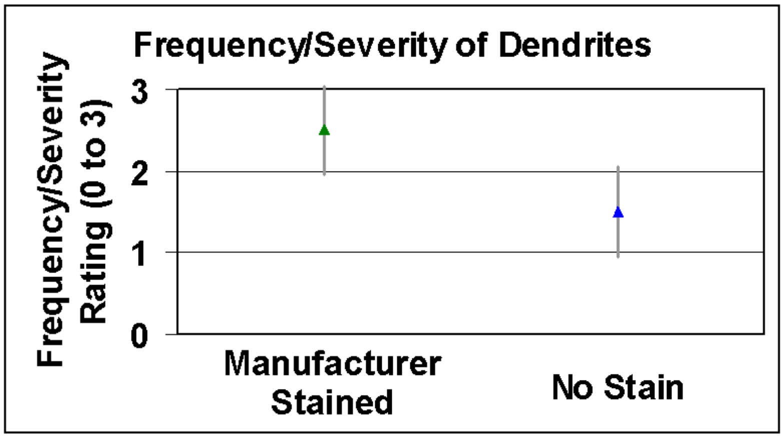

Figure 6 – Subjective average rating of the frequency and severity of dendrite formation in the stained and unstained test coupons. Standard deviations are shown by grey bars.

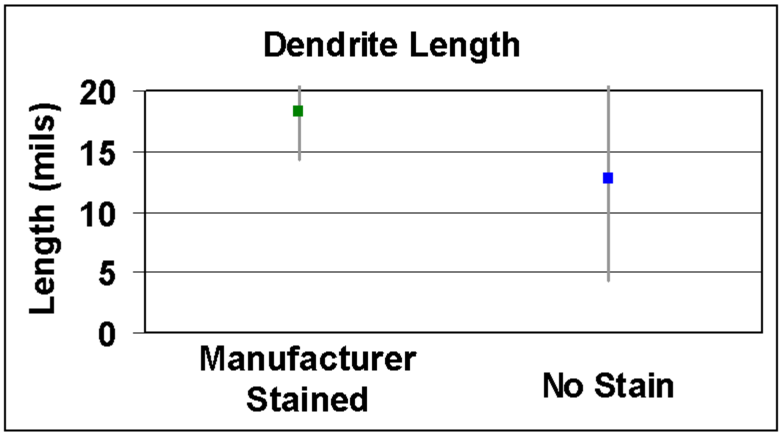

Figure 7 – Average length of dendrites for the stained and unstained test coupons. Standard deviations are shown by grey bars.

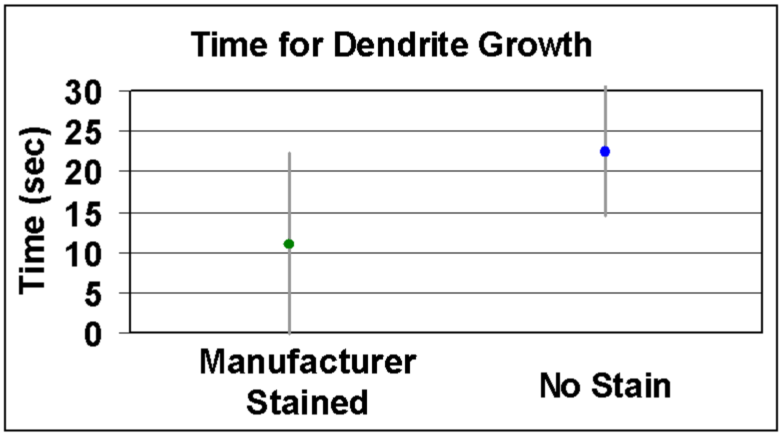

Figure 8 – Average time for dendrites to bridge the 20 mil electrode separation for the stained and unstained test coupons. Standard deviations are shown by grey bars.

Brown Stains:
The second type of stains discovered was also found on boards following component population and mass-reflow processes. Visual inspection revealed brown-colored staining on the white dielectric surface of RF PWBs, see Figure 9. As this condition had occurred multiple times, efforts were taken to both characterize the brown-colored residue and develop a procedure with which to remove the contamination. Once again, the discoloration was of concern due to the possibility of ionic contamination leading to electromigration that could cause the bridging of component pads and ultimately short electrical connections.

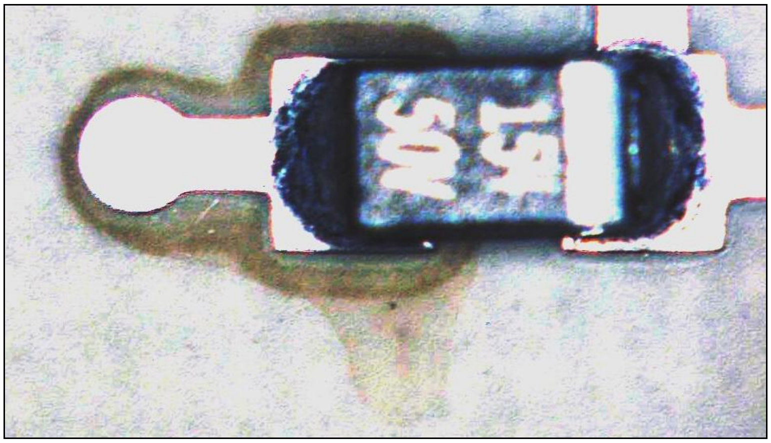

Figure 9 – Close-up photo of brown stain on assembled board.

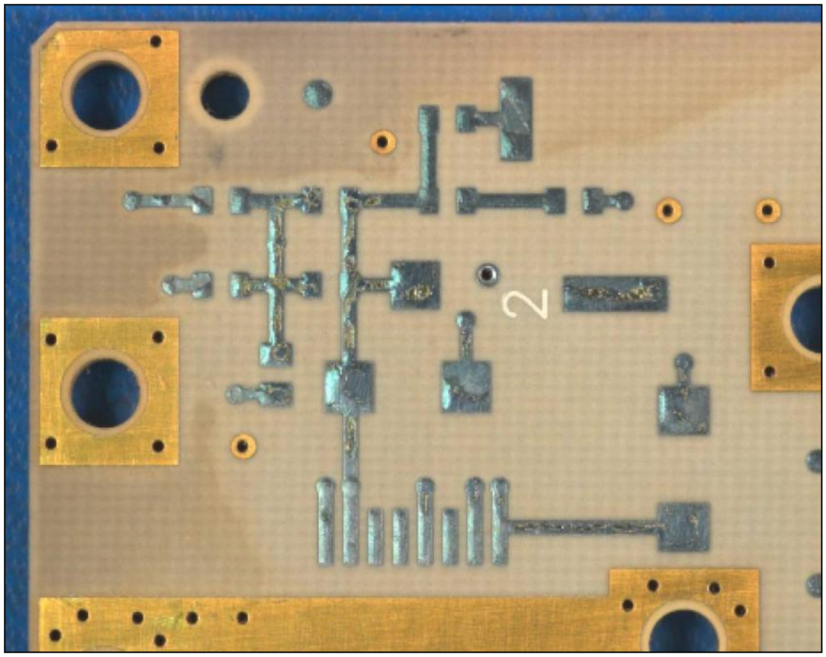

Figure 10: PWB following application of RMA solder flux and exposure to soldering heat.

Due to the color of the stains and their proximity to solder pads, rosin mildly active (RMA) solder flux was suspected. In an attempt at reproducing the brown-colored stain, flux was applied to a solder sample board, sent through a convection reflow oven two times, and then cleaned with IPA, see Figure 10. The brown-residue that remained after cleaning was then analyzed by Fourier Transform Infrared (FTIR) Spectroscopy.

To obtain the FTIR spectrum, the stained board was placed in a clean glass tray and submersed in a solution of 75% methylene chloride and 25% methanol until the PWB was completely covered. Then, the tray was placed into an ultrasonic bath for 20 minutes. The solvent was removed and the procedure was repeated until most of the stain was removed. A non-volatile residue (NVR) analysis was preformed on the combined extracts and found that 16μg/cm2 of residue was removed. A beaker blank was carried through all analyses as a control. Following NVR determination, the residue was characterized by FTIR by resuspending the residue in isopropyl alcohol and transferring the result to an aluminum-coated glass slide for analysis. The sample's spectrum was collected using 128 scans of the slide in reflectance mode using a clean portion of the slide as a background. Through FTIR characterization, the residue was determined to be consistent with rosin oil, see Figures 12 and 13.

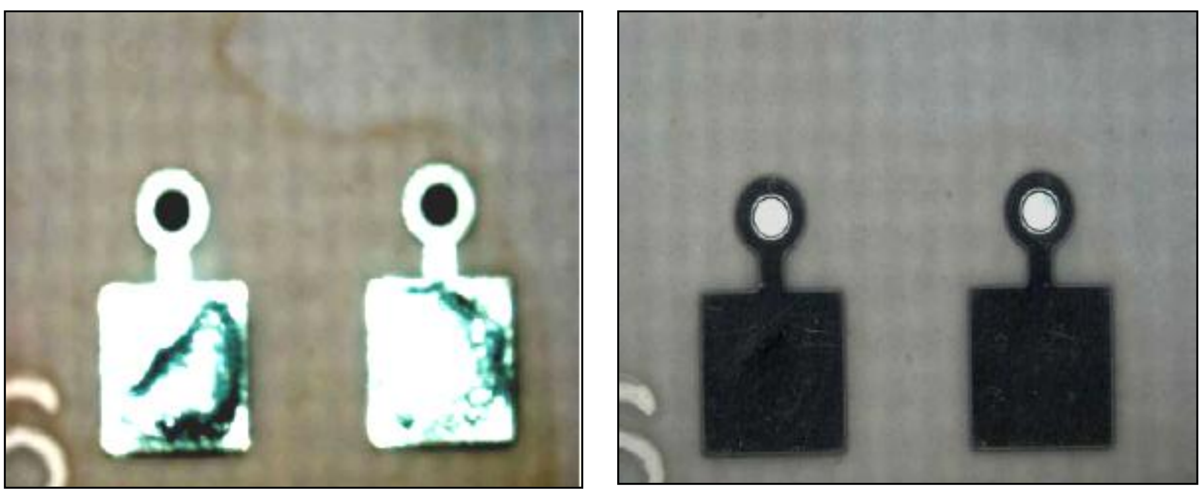

Figure 11 – Same brown stained area before (left) and after (right) methylene chloride/methanol solvent extraction.

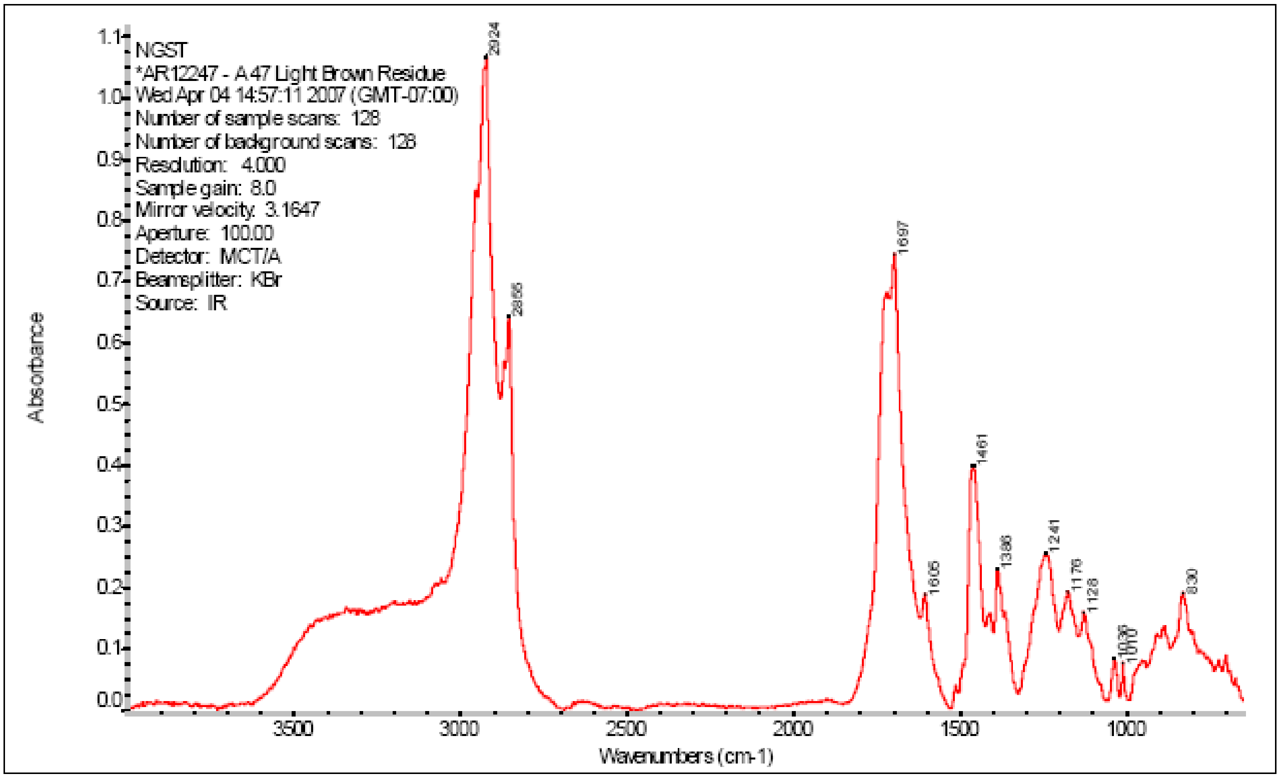

Figure 12 – FTIR spectrum of brown stain extracted from PWB.

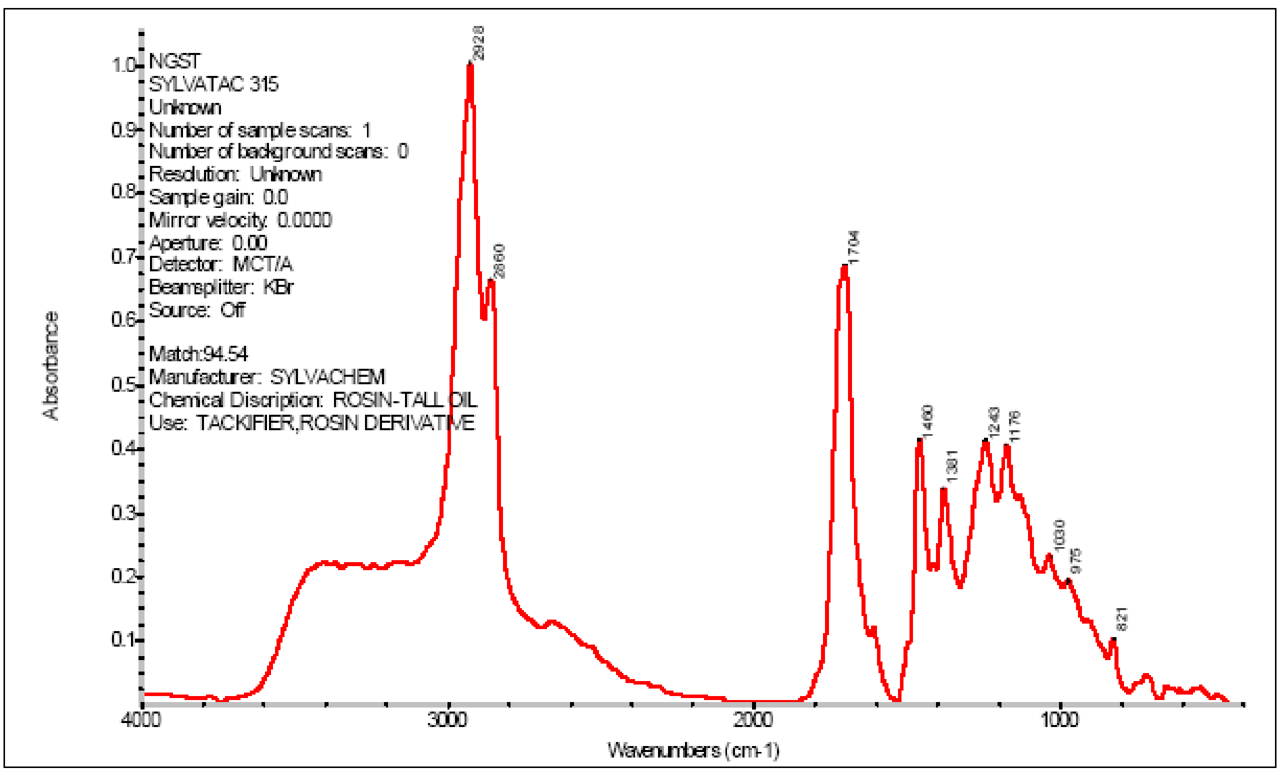

Figure 13 – FTIR reference spectrum of rosin oil.

Once the brown staining on the PWB surface was determined to be consistent with rosin oil, the question of stain removal naturally arose. The stains could be removed with the use of a cotton swab and appropriate solvent (acetone or 75% Methylene chloride / 25% Methanol). However, due to the aggressiveness of these solvents, other solvents were evaluated for efficacy. For removal of the brown discoloration, 4 different solvents were evaluated:

1. Isopropyl Alcohol (IPA)
2. Methyl ethyl ketone (MEK)
3. 1,1,1-Trichloroethane
4. Acetone
5. 75% Methylene chloride (CH_2Cl_2) / 25% Methanol

The solvents above are listed in order of aggressiveness, "1" being the weakest and "4" being the strongest. Each solvent was applied to a different cotton-tipped swab, and the swab was then rubbed back-and-forth across its own brown-stained area on the stained solder sample board. The results of this cleaning evaluation are summarized in Table 2.

Table 2 – Solvent cleaning effectiveness.

Solvent	**Result**	**Effectiveness** (1-5) 1 = poor, 5 = good
IPA	No visible change	1
MEK	No visible change	1
1,1,1-Trichloroethane	Slight removal of discoloration	2
Acetone	Stain largely-removed	4.5
75% Methylene chloride / 25% Methanol	Stain largely-removed	5

The 75% Methylene chloride/25% Methanol solution and acetone were both effective in removing the brown discoloration. Since acetone is a milder solvent, its use is recommended over the methylene chloride/methanol solution when cleaning populated boards.

Bleaching and Shadowing:

The final anomaly discovered involved what appeared to be dielectric with an underlying shadow. Figure 14 shows a portion of a PWB with a gold plated cutout. Surrounding the cutout area is what appears to be a shadow. It is believed that the majority of the laminate was bleached from bus bar etching. The product required the image/bus bars to be plated and etched prior to the nickel-gold plating process. The bars were placed in the location where the apparent shadow exists. After etching, the bare laminate was exposed to additional chemical processing. This processing included resist striping for etch protection, tin-lead stripping, and pumice scrubbing for the selective Ni/Au image. After the Ni/Au processing, the panels were again resist stripped and roughened by hand pumice scrubbing for the bus bar etch process. The PWB was then resist laminated to expose only the bus bars that needed to be removed. After etching the bus bars, you can see the color difference in the laminate where the copper protected the laminate from additional chemical processing and baking cycles. This appearance is related to the additional chemical processing that bleaches out the material. Although no reliability risk is associated with this condition, it often leads to questions when PWBs are initially inspected. Concerns regarding the possibility of contamination or the homogeneity of the material often must be addressed.

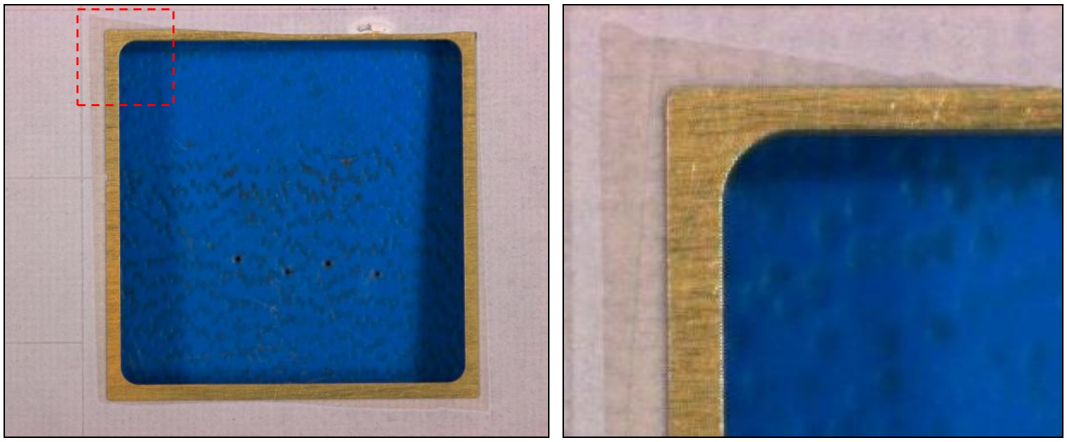

Figure 14 – Photo showing shadowing surrounding the gold plated cutout (detail is shown in the image at right). The white area in the upper right of the photo on the left is a laminate defect.

Conclusions

Several visual anomalies have been observed in light colored dielectrics. All anomalies were initially suspected to be due to unknown contaminants with unknown impacts to reliability. However, following investigation it was determined that none of the visual anomalies significantly affected performance or long-term reliability of the products. The first of the anomalies, plating solution stains, may facilitate dendrite growth to a limited extent, but any enhanced rate of growth did not appear to be significant. Dendrite growth is not believed to be a large risk with or without plating stains and no significant degradation to either performance or reliability is expected. The second of the anomalies, flux stains, were likewise determined to have negligible impact to reliability. The flux stains were able to be sufficiently removed by common solvents. The last anomaly discussed, bleached dielectric, was a natural consequence of the fabrication process and involves only minor changes to the laminate material with no impact to reliability. The common thread for these contaminants is that they were detectable only because of the nature of the dielectric material. Most of these anomalies would only have been detectable if they were on the surface of white dielectric. Although similar contaminants are likely on the surface of other board types, they are much harder to observe when the dielectric is darker in color. Brown flux stains on brown-colored polyimide, for example, are nearly impossible to identify. Early identification of these benign contaminants and process-induced anomalies will be a challenge for the hi-rel and aerospace industries in the coming years, especially as more applications require light colored laminate materials.

References

[1]IPC-2221: Generic Standard on Printed Board Design, IPC (1998).
[2]IPC-6012B: Qualification and Performance Specification for Rigid Printed Boards, IPC (2004).
[3]IPC-A-600F: Acceptability of Printed Boards, IPC (1999).
[4] IPC-9691: Users Guide for the IPC-TM-650, Method 2.6.25, Conductive Anodic Filament (CAF) Resistance Test (Electrochemical Migration Testing), IPC (2005).
[5]"Evaluating Conductive Anodic Filament Electrochemical Migration Test Results," Karl Sauter, IPC ECM Task Group 5-32e (2003).
[6]IPC-4103: Specification for Base Materials for High Speed/High Frequency Applications, IPC (2002).
[7]PWB Contamination and Reliability DOE," M. R. Weekes, Proceedings of the SMTA International Conference (2001).
[8]IPC-TR-476A: Electrochemical Migration: Electrochemically Induced Failures in Printed Wiring Boards and Assemblies, IPC (1984).
[9]"The Effect of Flux Chemistry, Applied Voltage, Conductor Spacing, and Temperature on Conductive Anodic Filament Formation," W. J. Ready and L. J. Turbini, Journal of Electronic Materials 31, 1208.
[10]ANSI/ J-STD-004: Requirements for Soldering Fluxes, IPC (1995).
[11]"Surface Insulation Resistance Testing of Soldering Pastes and Fluxes," R. Michalkiewicz, et al, Pan Pacific Microelectronics Symposium (2001).

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Introduction – Contamination

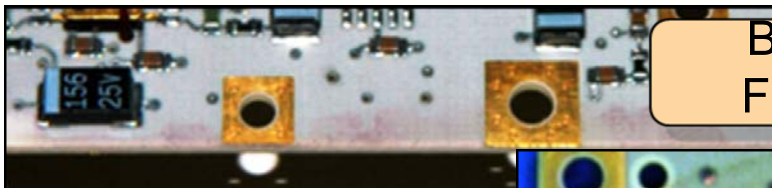
- PWBs intended for space applications are assumed to be 100% reliable.
- To ensure reliability, inspections to IPC class 3 and 3/A requirements are rigorous.
- Contamination poses several possible reliability risks.
  - Conductive particulates/films resulting in electrical shorts.
  - Promotion of electro-migration effects: dendrite or CAF growth
  - Alteration of dielectric constants affecting RF performance.

Contamination is a serious concern in space electronics applications.

Introduction – Observations

- PWBs were discovered with visible anomalies.
- Discolorations were highly visible due to white dielectric.

Purpose Stains:
Gold Plating Touchup



Brown Stains:
Flux Exposure

Darkening/Bleaching:
Multiple Processes

Several anomalies were discovered. Contamination was suspected.

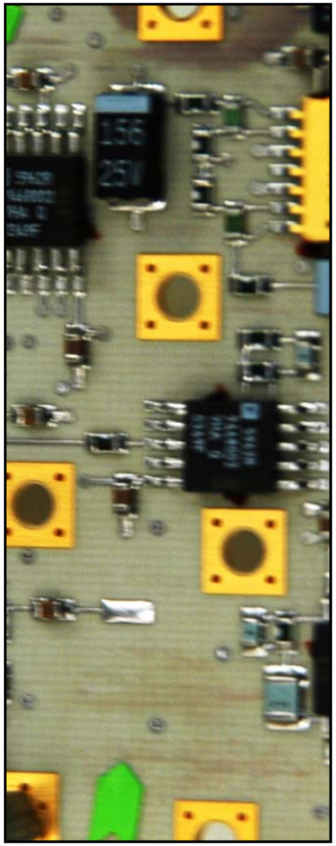
Introduction – Concerns

- Immediate performance impacts
  - Conductive bridging
  - Material changes leading to RF performance degradation
- Latent reliability impacts
  - Dendrite formation leading to conductive bridging
  - Conductive anodic filament growth leading to conductive bridging
  - Material changes leading to structural degradation
  - Corrosion concerns
  - Outgassing concerns (space product)

Foreign material and contamination pose several possible concerns.

Purple Stains – Observation

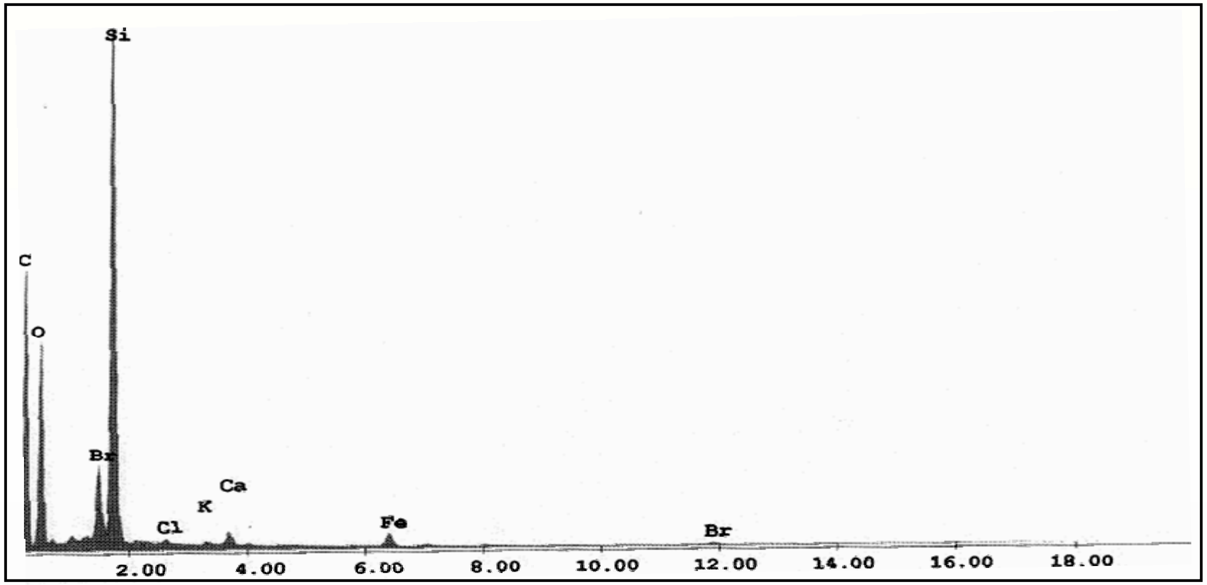
- Stains were discovered on populated multilayer PWBs with Sn-Pb surface finishes and Au mounting locations.
- All PWBs were inspected prior to assembly.
- Conjectured to be Au plating solution residue from touchup.



Gold plating touchup was suspected in purple staining of PWBs.

Purple Stains – Analysis

- Energy dispersive x-ray (EDX) spectroscopy was performed to determine if stained laminate was conductive.
  - No metals were found in any significant concentration.



Purple stains were not conductive.

Purple Stains – Evaluation

- Dielectric withstanding voltage (DWV) tests showed no leakage current between closely spaced electrodes.
- Ion Chromatography and Inductively Coupled - Plasma Mass Spectrometry (ICP-MS) indicated elevated levels of ionic contaminants.

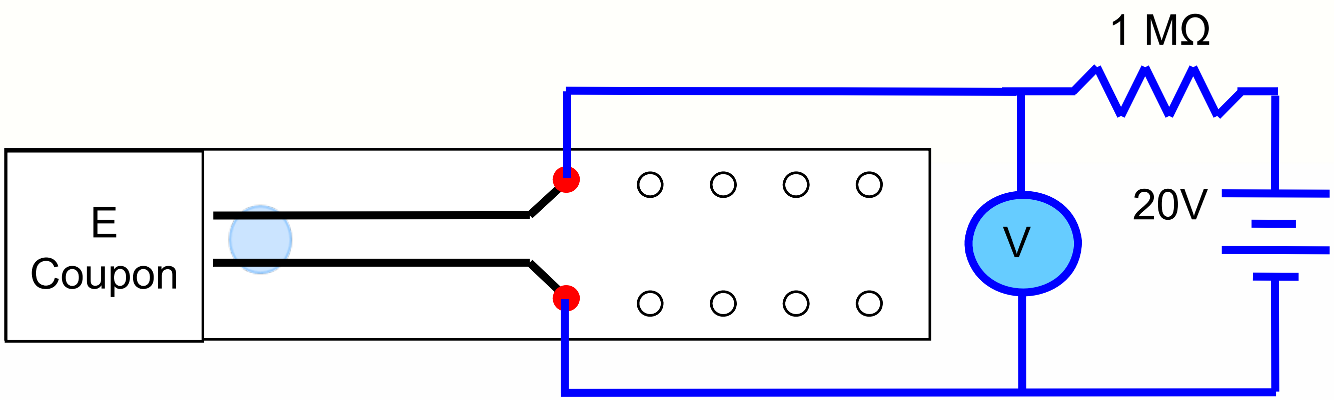
Parameter	In Unstained Board Sample (µg/cm²)	In Stained Board Sample (µg/cm²)
Metals		
Aluminum	Major	Major
Chromium	0.32	0.47
Iron	1.5	5.1
Nickel	0.41	0.74
Copper	Major	Major
Zinc	Major	Major
Tin	0.16	0.39
Antimony	0.26	0.34
Gold	0.42	2.2
Lead	0.17	0.45
Cations		
Lithium	ND < 0.08	ND < 0.08
Sodium	0.39	1.4
Ammonium	ND < 0.08	1.0
Potassium	0.29	0.43
Calcium	ND < 2.5	ND < 2.5
Magnesium	ND < 0.3	ND < 0.3
Anions		
Fluoride	ND < 0.08	ND < 0.08
Chloride	0.45	0.73
Bromide	0.10	0.30
Nitrate	ND < 0.8	ND < 0.8
Phosphate	ND < 3	ND < 3
Sulfate	0.45	5.5

ND = Not detected

Ionic contamination was slightly elevated.

Purple Stains – ECM Testing

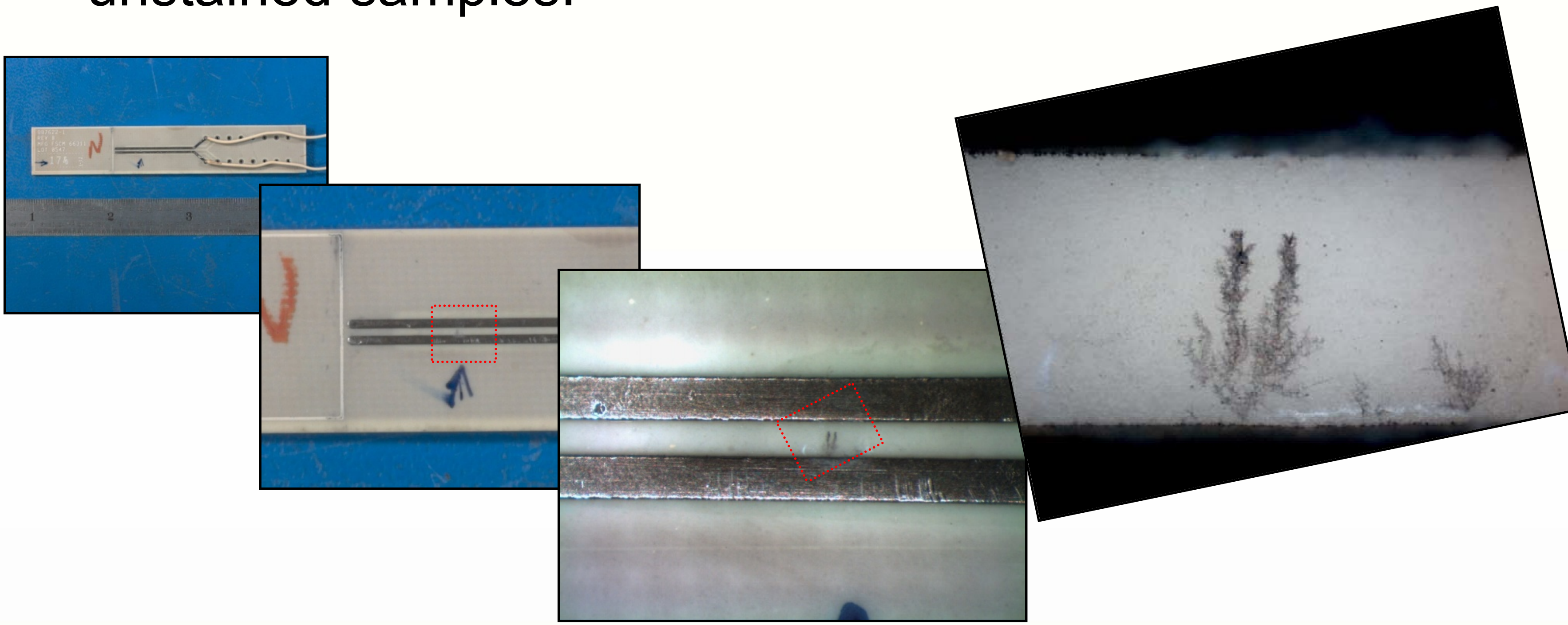
- Electrically biased water droplet test was performed to assess any increased dendrite formation risk.



Biased water droplet test was performed to assess dendrite risk.

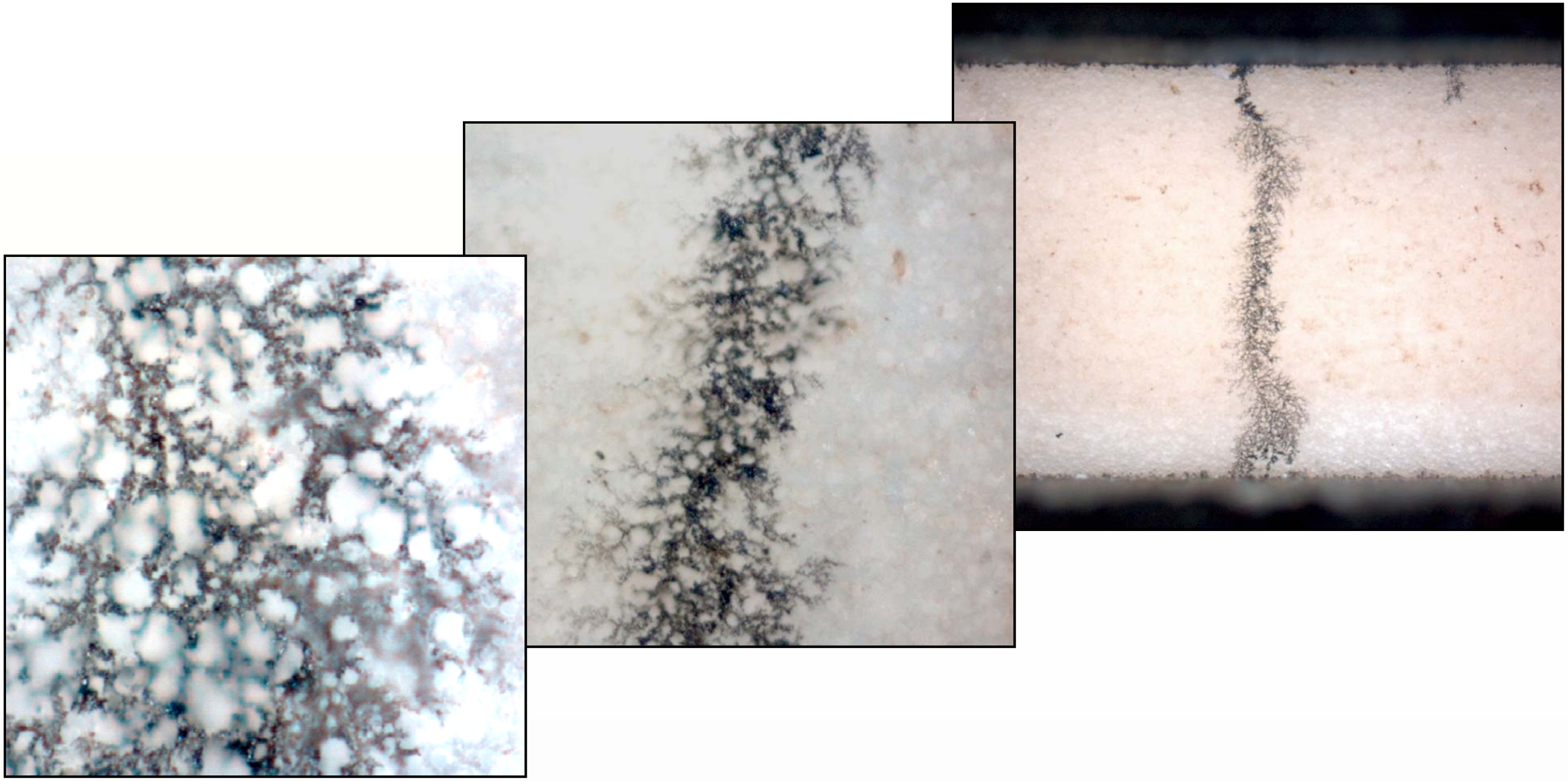
Purple Stains – Dendrite Formation

- Dendrite formation occurred on both stained and unstained samples.



Dendrites formed on both stained and unstained samples.

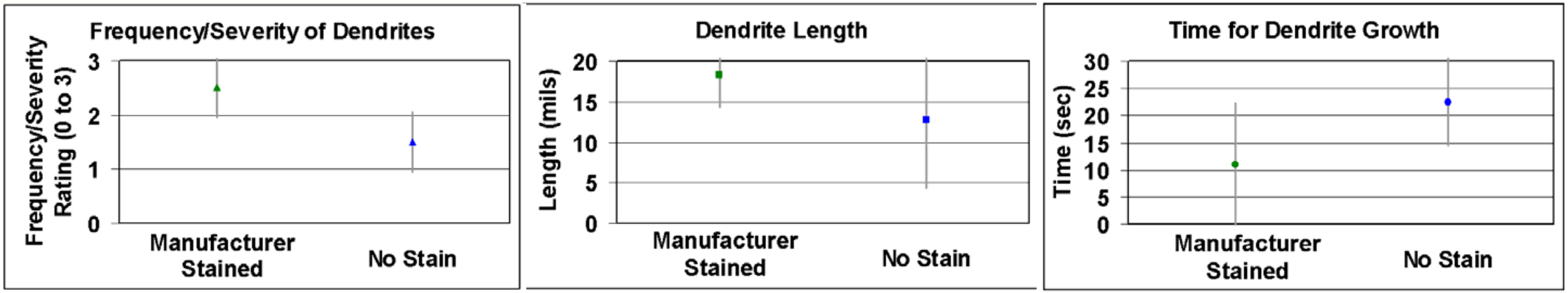
Purple Stains – Dendrite Formation



Dendrites easily bridged the electrodes.

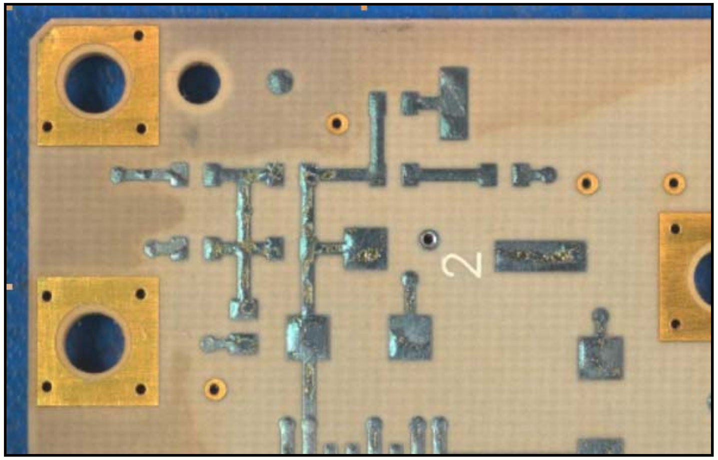
Purple Stains – ECM Testing

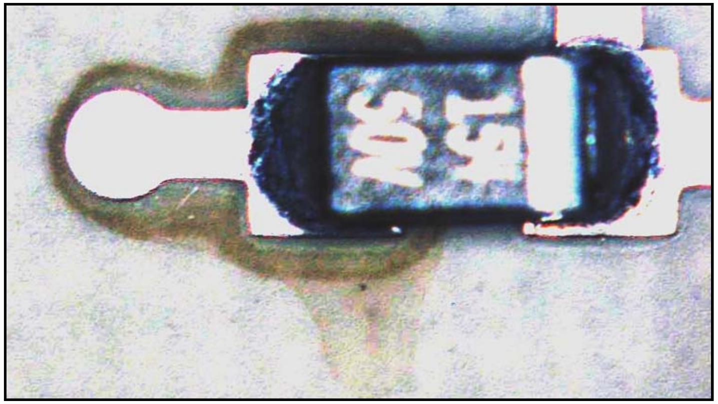
- Although often subjective, stained coupons seemed to grow more dendrites, a longer distance, in a shorter period of time than the unstained control group.
- However, no differences between the two groups were significant.



Purple stains due to gold plating touchup do not pose a reliability risk.

Brown Stains – Observation



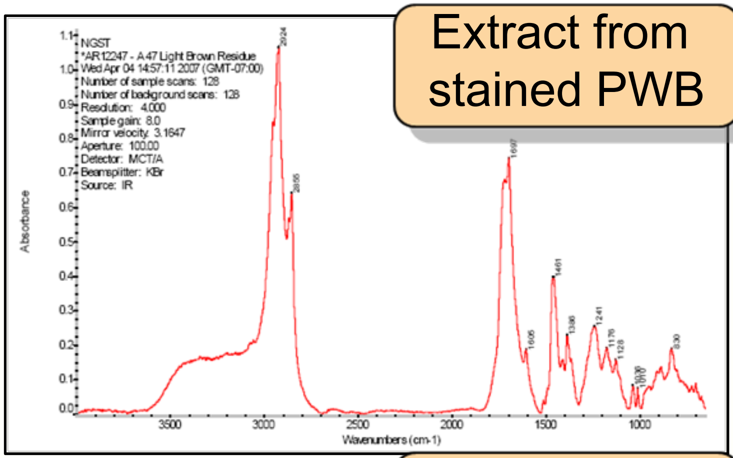


- Visual inspection revealed brown-colored staining on the white dielectric surface of RF PWBs.
- Again, the discoloration was of concern due to the possibility of ionic contamination.
- Due to the color of the stains and their proximity to solder pads, rosin mildly active (RMA) solder flux was suspected.

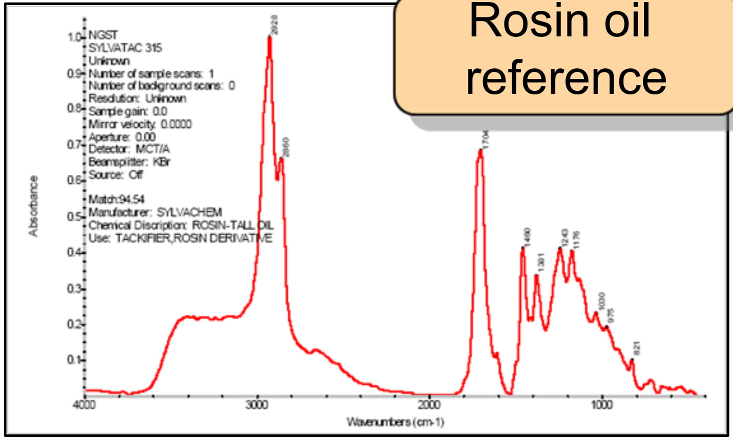
Solder flux residue was suspected to cause brown stains.

Brown Stains – Analysis

- In an attempt at reproducing the brown-colored stain, rosin mildly active (RMA) flux was applied to a solder sample board, sent through a convection reflow oven two times, and then cleaned with IPA.
- The brown-residue that remained after cleaning was then analyzed by Fourier Transform Infrared (FTIR) Spectroscopy.



Extract from stained PWB



Rosin oil reference

FTIR confirmed flux as the cause of the brown stains.

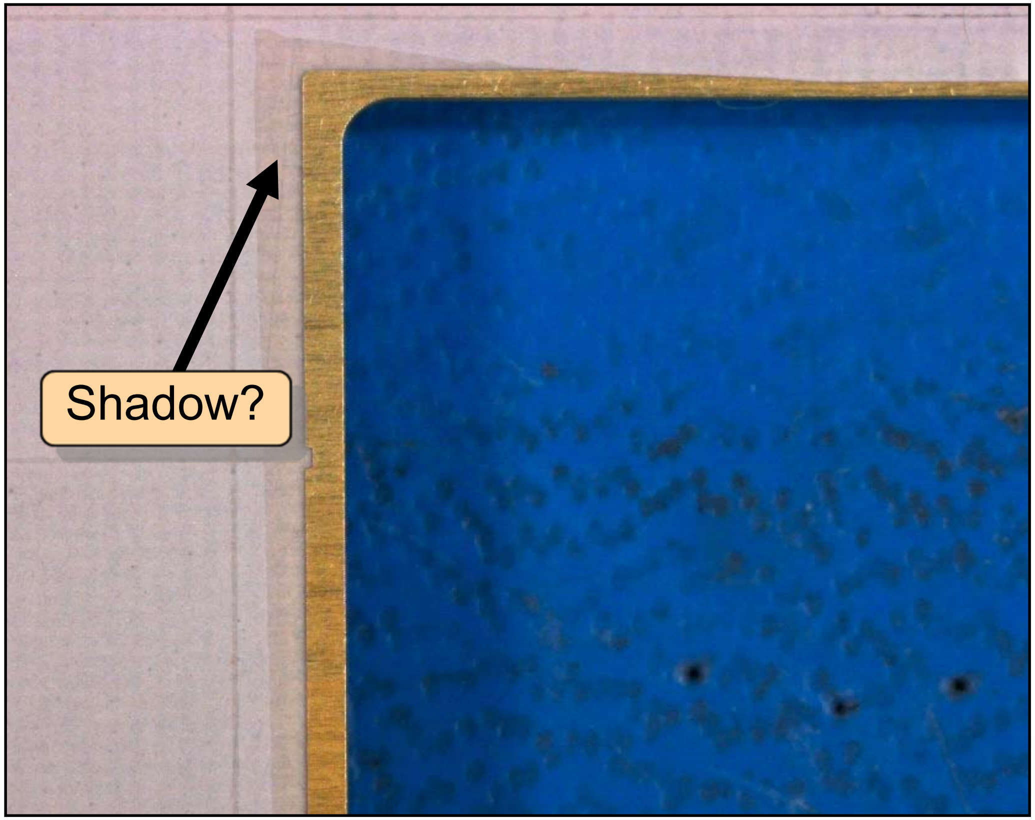
Brown Stains – Removal

- For removal of the brown discoloration, 5 different solvents were evaluated.
- The 75% Methylene chloride/25% Methanol solution and acetone were both effective in removing the brown discoloration.

Solvent	Aggressiveness 1 = Least, 5 = Most	Result	Effectiveness 1 = Poor, 5 = Good
Isopropyl Alcohol (IPA)	1	No visible change	1
Methy ethyl ketone (MEK)	2	No visible change	1
1,1,1-Trichloroethane	3	Slight removal of stain	2
Acetone	4	Stain largely removed	4.5
75% Methylene chloride (CH_2Cl_2) / 25% Methanol	5	Stain largely removed	5

Acetone is recommended when cleaning populated boards.

Dielectric Bleaching – Observation



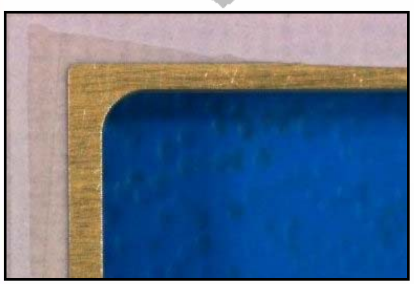
- An anomaly was discovered that appeared to be dielectric with an underlying shadow.
- It is believed that the majority of the laminate was bleached from bus bar etching.

"Shadowing" has been observed near gold plated areas.

Dielectric Bleaching – Processing

- Bus bar etching involves multiple process steps.

1. Bus bars placed (shadow location)
2. Laminate etched
3. Resist stripped
4. Tin-lead stripped
5. Bus bars etched
6. Pumice scrubbed
7. PWB resist laminated
8. Bus bars removed

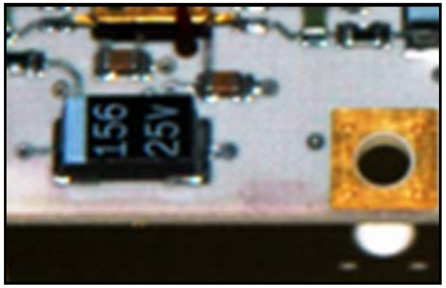


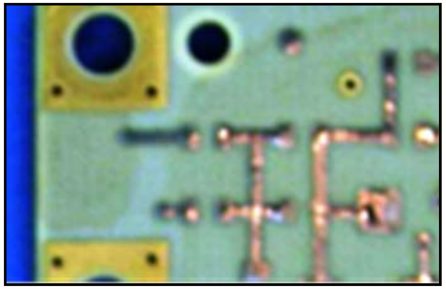
- The unprotected dielectric was bleached.
- Although no reliability risk exists, concerns regarding the contamination and material homogeneity arise during inspection.

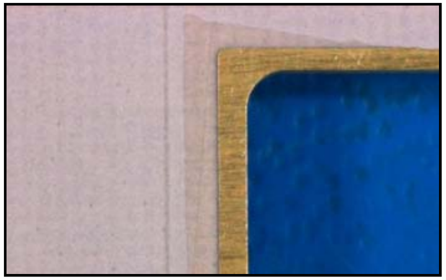
"Shadowing" resulted from processing that bleached the dielectric.

Conclusions

- None of the visual anomalies significantly affected performance or reliability.
- Contaminants would not have been observed on darker dielectric materials.
- Early identification of these benign contaminants and process-induced anomalies will be a challenge for the hi-rel and aerospace industries in the coming years, especially as more applications require high speed, light colored laminate materials.







Anomalies were detectable only due to the light colored dielectric.