A Plasma Deposited Surface Finish for Printed Circuit Boards

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Abstract

This paper will discuss a new approach to the final finishing for the PCB industry which is based on the use of an ultra-thin fluoropolymer film as a protective coating to preserve solderability of the circuit board between manufacture and assembly. The coating has been shown to extend the shelf life of the PCB by preventing oxidation and corrosion, and ensures excellent solderability during assembly. The fluoropolymer coating is applied using a dry plasma deposition process, which eliminates the use of harsh chemicals and waste streams associated with other surface finishes. The coating has been applied directly on to copper, or can be used in conjunction with other surface finishes to act as a corrosion inhibitor when specific properties are required, such as resistance to creep corrosion or tarnish.

Significant testing has been performed on the fluoropolymer coating to demonstrate its capability as a surface finish for the PCB industry. The results of solderability testing, solder joint reliability testing and corrosion protection will be discussed.

Introduction

Over the past decade the electronics industry has faced challenges to existing manufacturing processes as it responds to changes in legislation and guidelines that impact electronic products. Additionally, technology continues to evolve and demands products that are smaller and faster and cheaper to produce. The changes in electronics manufacturing processes are particularly apparent in printed circuit board (PCB) manufacture and assembly. The introduction of RoHS Pb-free requirements for electronics and the ever increasing complexity of SMT components are two factors that have greatly impacted the final surface finish of PCBs. Sn/Pb HASL, once the de facto standard for surface finishing, has been rapidly replaced by a range of alternatives, each with particular advantages and drawbacks.

For example, organic solderability preservatives (OSP) can be very cost effective in high volume manufacturing, but tend to suffer from short shelf life and difficulty with in-circuit testing and electrical contacts. Immersion silver (ImAg) has been adopted by many manufacturers due to ease of processing and relatively low cost, but concerns remain about long term reliability due to creep corrosion and voids in solder joints. Electroless nickel immersion gold (ENIG) has enjoyed popularity for higher end applications because of its very good shelf life and excellent solderability. However, this finish has drawbacks, primarily cost and reliability concerns such as "Black Pad" if the process chemistry is not carefully controlled[1].

The use of a plasma deposited fluoropolymer coating as a solderable final surface finish for printed circuit boards has recently been introduced. The plasma finish was shown to exhibit exceptional corrosion resistance while maintaining good solderability for SMT and through-hole soldering. This novel surface finish has the potential to change the PCB manufacturing process, drastically shrinking environmental impact by reducing water consumption and heavy metals usage.

The environment in which electronic products are now expected to regularly operate is growing ever harsher due to increased pollution levels and the increasing use of these products in high heat, high humidity areas. Failure of electronic products due to corrosion caused by environmental exposure is becoming increasingly common. One particular type of corrosion that has begun to manifest itself is creep corrosion. This failure mechanism is of particular concern as it can lead to catastrophic failure in products either by causing electrical shorts between adjacent tracks or electrical opens in conductive tracks. While nearly every final surface finish has been shown to exhibit creep corrosion in the most aggressive atmospheres, immersion silver is generally understood to be the most susceptible surface finish to this failure mechanism. The plasma deposited fluoropolymer coating can serve as an excellent inhibitor to creep corrosion across a range of surfaces.

Plasma Deposition Method

The use of gas plasma as a processing technique can be a very efficient and powerful tool. Plasma processing is used extensively in industries as varied as semiconductor manufacturing, automotive component manufacturing and medical device fabrication. Plasma etching is currently employed in the PCB fabrication industry to achieve de-smear of drilled vias, where it routinely achieves greater than 75% uniformity in etch rate performance across large PCB panels. Plasma surface activation is also used to treat PTFE boards and some packaging substrates to improve adhesion of underfill and conformal coating materials[2]. Plasma processing has many advantages over traditional wet chemical processing, such as the lack of chemical residues from rinsing, the lack of surface tension issues, and excellent process control and reproducibility.

The use of plasma as a deposition technique represents a novel approach for coating PCB panels. In a conventional plasma cleaning process, a gas such as oxygen or argon can be used to chemically or physically etch a surface. In the plasma deposition process, a reactive precursor gas is used which can polymerize in the conditions generated in the plasma chamber. The growth of the polymer film can be controlled by adjusting input parameters, and the continuity and quality of films deposited using this method has been well documented[3-5]. In the case of the plasma finish for PCBs, a halohydrocarbon precursor gas is introduced to a plasma chamber that has been specifically designed for the treatment of large format PCB panels. Striking the plasma in the chamber activates the precursor gas and a thin coating of a dense, highly cross-linked fluoropolymer film is deposited across the entire surface of the PCB panel. An example of a plasma deposition system designed for high volume production of plasma finished PCBs is shown in Figure 1. This system is manufactured by Nordson March and is capable of coating 13 large format PCB panels in parallel.

Figure 1- Plasma deposition system suitable for the volume production of plasma finished PCB panels

Plasma Finish Solderability

The plasma finish has been developed to deliver consistent and reliable Pb-free solderability. An extensive test plan has been carried out to determine the plasma finish's suitability for use as a solderable final surface finish for PCBs. The thin fluoropolymer coating does not need to be removed prior to assembly as the combined action of the acidic flux and the heat during reflow dissolves the coating in the areas where the joint is to be formed. The action of the flux is limited to the areas where the solder paste has been printed, and in solder spread testing very little flow of the solder is observed. Optical micrographs of solder joints and cross sectional analysis are shown in Fig 2. The solder shows good coverage of the copper pads, although the solder does not flow across the surface of the fluoropolymer to wet the entire pad.

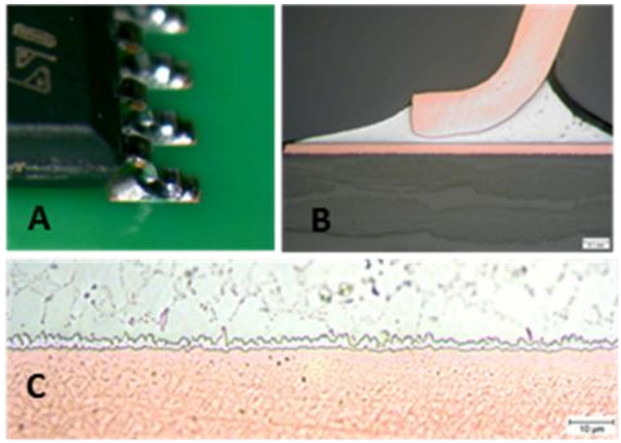

Figure 2 – Component soldered on a plasma finish board. Optical microscopy image of component on board (A), microsection of component leg and solder joint (B), microsection showing continuous Cu_6Sn_5 intermetallic between copper pad and solder (C).

Solderability of the plasma finish has been confirmed using wetting balance. The wetting balance is a quantitative method to assess the ability of a surface to be wet by molten solder. Test samples are brought into contact with a globule of molten solder, and the change in forces applied on the sample is recorded. Initially, the sample will be repelled and a negative force recorded, then as the sample is wetted by the solder a positive force will be recorded. Key parameters for wetting balance testing are time to buoyancy, maximum force, and time to 2/3 maximum force. The results of the wetting balance testing shown below in Figure 3 confirm that the fluoropolymer does not inhibit solderability in any way.

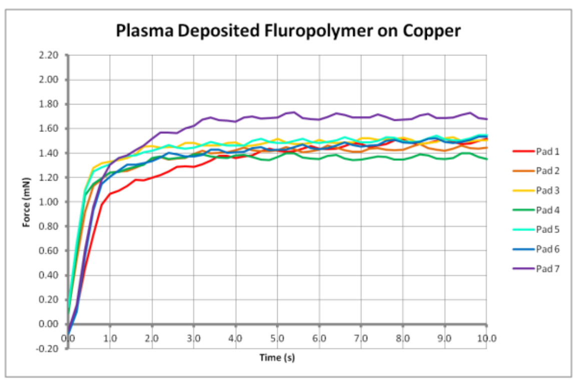

Figure 3 – Wetting balance curves for plasma finished copper PCB samples

Solder Joint Reliability

The strength and reliability of the solder joint between surface mount components and a PCB coated with the plasma finish was assessed using ultimate shear strength testing. The test vehicle for this experiment was a PCB with a series of twenty 0603 resistors assembled using SAC 305 solder under standard Pb-free reflow conditions. This testing was completed at the National Physics Laboratory (NPL) in the UK. The stand-off height of the chisel tool above the PCB surface was 80mm, and the width of chisel tool was 2mm for 0603 resistor. During each test, the shear tool was moved forward at a defined speed of 100mm/s against the test component, and the force was monitored until the solder joint attachment broke. The shear tester was a Dage Series 4000, with a DS100 testing head. The initial shear strength results for 0603 resistors on the plasma finished board were comparable to the results from boards assembled with OSP and ENIG surface finishes. The experiment was repeated for components that were assembled on the 2nd, 3rd, 4th, and 5th reflow cycle and no significant difference was observed (Figure 4).

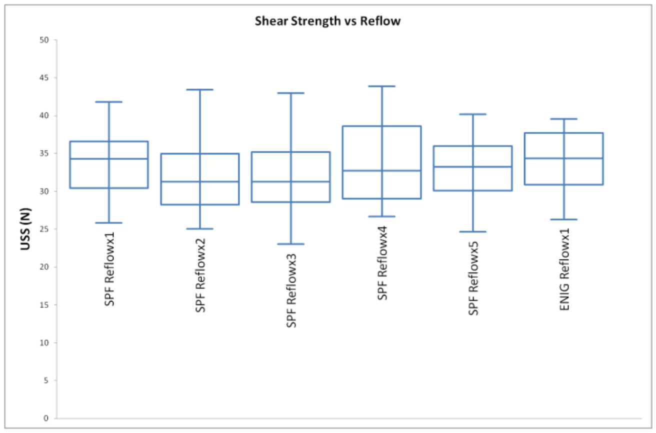

Figure 4 – Ultimate shear strength of 0603 resistors over multiple reflow cycles (each point is average of 40 shears).

The long term solder joint reliability was determined by subjecting assembled PCBs to accelerated lifetime testing. The experimental design is depicted in Figure 11. Plasma coated PCBs were assembled using standard Pb-free reflow processes. A set of reference boards prepared with an ENIG surface finish was included in the test as a comparison. The boards were then placed in an oven at 150C and samples were removed every 200 hours for a total test time of 1000 hours. At the completion of the test the sample set was split with half of the aged samples going for cross section analysis and the remaining samples for shear testing.

For each aging time period a selection of solder joints was cross sectioned and the composition of the intermetallic layers were analyzed using optical microscopy and energy dispersive X-ray analysis (EDX). The optical microscopy images of the starting (t=0) samples shows a clear Cu/Sn intermetallic layer at the interface between the copper land pad and the SAC305 solder. The composition of the layer was determined using EDX and was found to be 39.5% Cu and 60.5% Sn, which corresponds to a Cu_6Sn_5 intermetallic.

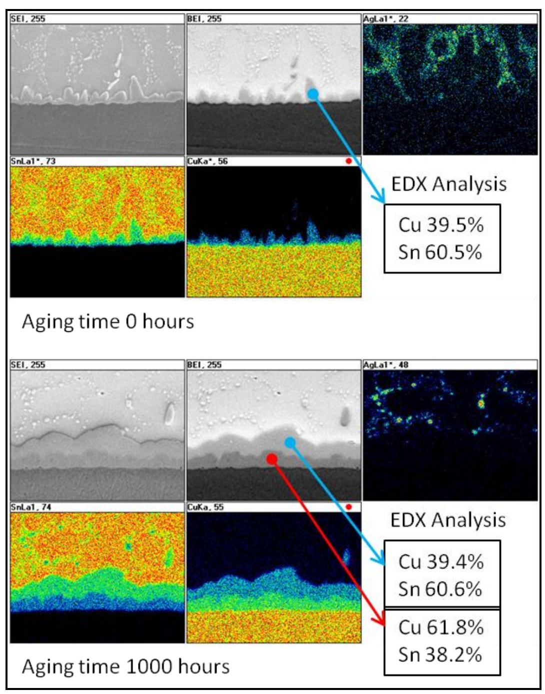

Figure 5 – Cross sectional EDX analysis of thermally aged samples

Extended thermal aging of the test samples resulted in the growth of the intermetallic layer, and in the development of a second intermetallic at the interface of the copper pad, as shown in Figure 12. The second layer was found to have a composition of 61.8% Cu and 38.2% Sn, which corresponds to the weaker Cu_3Sn intermetallic. The growth rate of these layers was determined by mapping the layer thickness against time at the elevated temperature and correlates well with the literature.

The strength of the solder joints was assessed using shear testing of 0603 resistors, using the procedure outlined previously. The shear test results show a slight degradation in the strength of the joint, which would be expected due to the growth of the weak Cu_3Sn intermetallic layer. The ENIG reference samples also showed a reduction in the strength of the joints, which was in fact more pronounced than the reduction observed for the plasma finished samples (Figure 6).

Plasma Finish Corrosion Protection

Electronic products are increasingly being manufactured and used in aggressive environments. The primary manufacturing centers for electronic goods are now in areas where the combination of high humidity, high temperatures and high pollution levels can result in significant premature failure rates. The plasma finish fluoropolymer coating provides exceptional protection to the PCB against corrosion and surface oxidation. This level of protection can be observed by exposing coated and uncoated PCB samples into corrosive atmospheres, for example the high sulphur dioxide atmosphere generated above a buffered sodium sulphite solution at 40°C. The SO_2 gas exposure will rapidly degrade exposed copper and ImAg surfaces but has virtually no impact at all on the plasma finish fluoropolymer protected samples.

In mixed flowing gas (MFG) testing PCBs coated with the plasma finish outperformed all reference samples, including OSP, ImAg and ENIG. The purpose of MFG testing is to simulate corrosion due to exposure to aggressive environments. Printed circuit boards coated with the plasma deposited fluoropolymer were subjected to a Class III environment Mixed Flowing Gas test, consisting of 100ppb of H_2S, 200ppb of SO_2, 200ppb of NO_2 and 20ppb of Cl_2, for a period of 20 days and were compared against unprotected printed circuit boards finished with ImAg, OSP, and ENIG. The fluoropolymer coated samples produced virtually no corrosion (<5% of the surface area), while the unprotected reference PCBs were all substantially corroded.

Creep Corrosion Prevention

Creep corrosion is a specific type of corrosion that is currently of particular concern to the electronics industry as it can lead to catastrophic failure in products either by causing electrical shorts between adjacent tracks or electrical opens in conductive tracks. Creep corrosion has been very well studied over the last 5-7 years, and the failure mechanism is now fairly well understood. Creep corrosion manifests as blooms of conductive material that grow outward, across the surface of the PCB from exposed metal contacts. The composition of the growing corrosion product has been shown to be primarily copper sulphide (Cu_2S). The failure is caused by excessive levels of sulphur in the atmosphere, combined with moisture to create a highly corrosive environment at the surface of the electronic assembly. Examples of creep corrosion are shown in Figure 6 (Source: R. Schueller, DfR). As the fluoropolymer plasma finish has been shown to protect surfaces from sulphur induced corrosion, further testing was carried out to assess the impact of the coating on preventing creep corrosion.

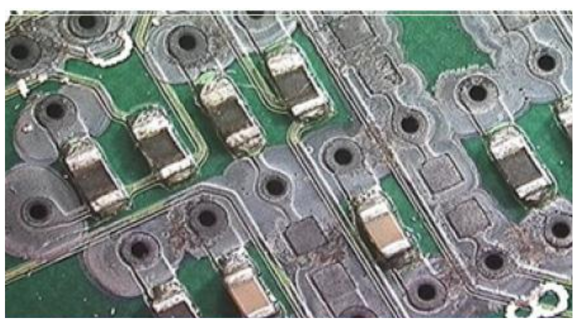

Figure 6 – Creep corrosion on ImAg finished PCB

Chavant Clay creep corrosion testing has been performed on a series of samples in order to determine the effectiveness of the fluoropolymer coating at inhibiting creep corrosion. The Chavant Clay creep corrosion test was performed by heating 50g of Chavant J-525 sulphur bearing clay to the point of bubbling in a microwave oven. The clay is then immediately placed into a glass desiccator with the test samples and 5ml of deionized water and the chamber is sealed. The clay is re-heated twice daily and replaced with new clay every 48 hours. The samples are inspected regularly under a microscope for creep corrosion and the test is run until the uncoated reference samples exhibit severe corrosion. The test set consisted of bare copper, OSP and ImAg, and fluoropolymer over copper PCBs, and all testing was performed after the samples had been subjected to one Pb-free reflow to ensure that the fluoropolymer would survive the harsh thermal excursion. Micrographs of the test samples after Chavant Clay testing are presented in Figure 7. Creep corrosion can clearly be observed in all samples at the metal / solder mask interface except the plasma deposited fluoropolymer coated sample (D).

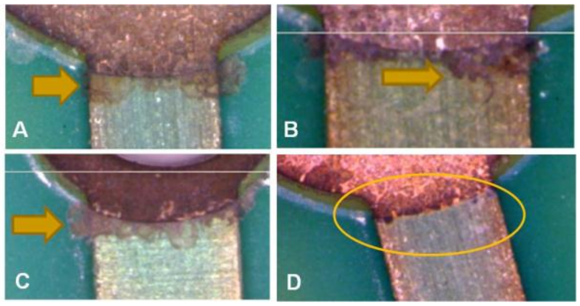

Figure 7 – Micrographs of (A) bare copper, (B) OSP, (C) ImAg showing creep corrosion at the solder mask interface and (D) fluoropolymer coated copper without creep corrosion

The fluoropolymer coated copper PCB show a significant improvement over the other samples. The copper does not appear to have been extensively corroded, and very little, if any, creep of the corrosion product is evident. Even at the copper / solder mask interface almost no creep corrosion was observed, as circled in Figure 7. This result stands in contrast to the bare copper samples. It is clear that the fluoropolymer coating has effectively inhibited the onset of creep corrosion.

In order to further test the effectiveness of the fluoropolymer coating at inhibiting creep corrosion, the coating was tested as an over coat on immersion silver finished PCBs. The fluoropolymer coating was applied either before or after a lead free reflow cycle using the same deposition recipe that was used to coat the copper samples, with an average coating thickness of approximately 40nm. The PCBs were then placed into the corrosion chamber, along with several bare ImAg samples for reference, following the test method detailed above. The results of the test, shown in Figure 8 below, clearly show that the plasma deposited fluoropolymer coating is able to prevent tarnish and creep corrosion on the ImAg sample.

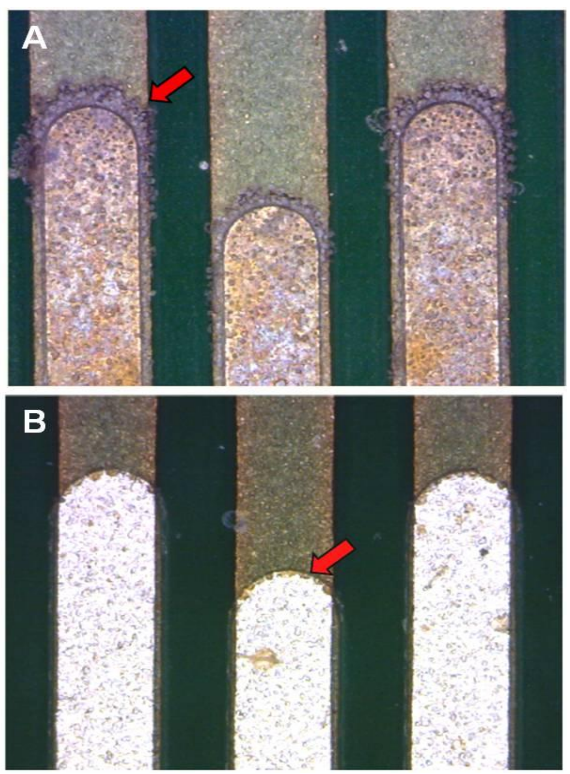

Figure 8 – Micrographs of solder mask defined features on (A) bare ImAg and (B) fluoropolymer coated ImAg after 7 days of Chavant Clay creep corrosion testing

The use of the plasma deposited fluoropolymer to prevent creep corrosion on immersion silver finished PCBs adds several new possibilities for the integration of this material into the manufacturing process flow. The coating can be applied as a top coat by the PCB fabricator, prior to assembly. Alternatively, the coating can be applied by the electronics manufacturer after the board has been assembled. In this case the coating would act more as a conformal coat.

Conclusions

This novel plasma finish is a plasma polymerised fluoropolymer which has been developed as an alternative to plated surface finishes for the PCB industry. The fluoropolymer plasma coating allows for reliable Pb-free solder joints to be made directly to the Cu surface of a PCB, without the need to remove the coating before soldering. We believe that the use of a plasma deposited fluoropolymer coating can effectively inhibit the onset of creep corrosion in electronic assemblies. The corrosion prevention properties of fluoropolymers are well known, and the impact of these materials on the corrosion of printed circuit boards has been documented in many corrosion tests. The use of plasma deposition to apply these coatings offers many advantages, including ease of processing, lack of solvents or waste chemicals, and uniformity of coating coverage.

Acknowledgements

The authors would like to thank DfR Solutions, and Randy Schueller in particular, for performing the Chavant Clay creep corrosion testing and analysis. The authors would also like to acknowledge Nordson March for their support in the development of high volume manufacturing plasma systems for the deposition of the fluoropolymer coatings used in this paper.

References

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A Plasma Deposited Surface Finish for Printed Circuit Boards

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Semblant™

Outline

- Introduction
- Plasma Deposition Method
- Fluoropolymer Coating
- Fluoropolymer Solderability
- Solder Joint Reliability
- Corrosion Protection
- Conclusions

Plasma Deposition Method

The Plasma Finish is thin polymer coating applied to the entire surface of a PCB to protect the board and preserve solderability.

Manufacturing friendly process

- Small footprint (2.5m x 2.7m)
- A fast, high throughput system
- Clean, dry, room temp process
- Environmentally Friendly
  - No Hazardous Gases
  - No Hazardous Waste

Excellent process control

Plasma Polymerization

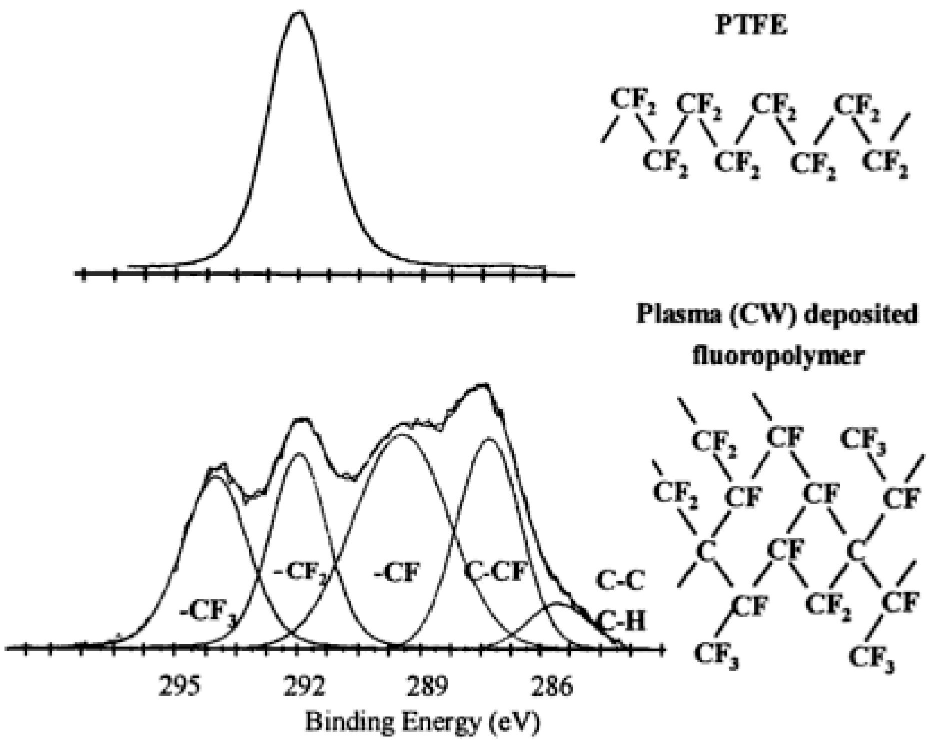


Figure 2.1. Chemical structure and ESCA (Electron Spectroscopy for Chemical Analysis) C1s spectra for PTFE and a fluorocarbon coatings plasma-deposited in CW conditions.

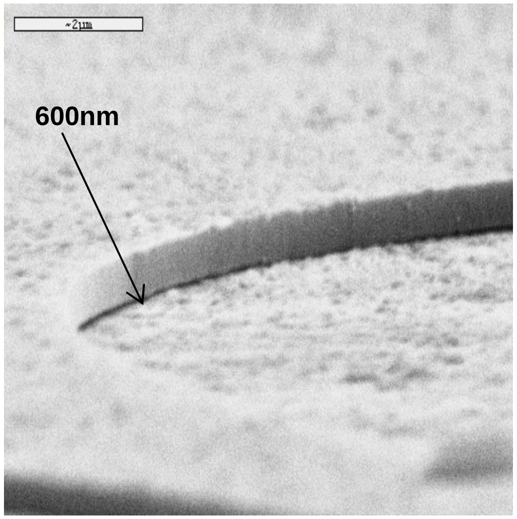
The plasma polymer is a unique class of material

- Conditions in the plasma chamber allow formation of structures that cannot be made using traditional polymerization reactions
- Plasma polymers tend to be highly cross-linked, randomly branched and contain un-reacted functionality

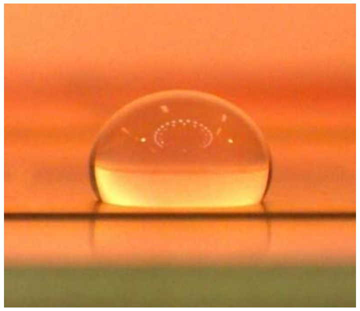
The Plasma Finish is a hybrid PTFE-like material

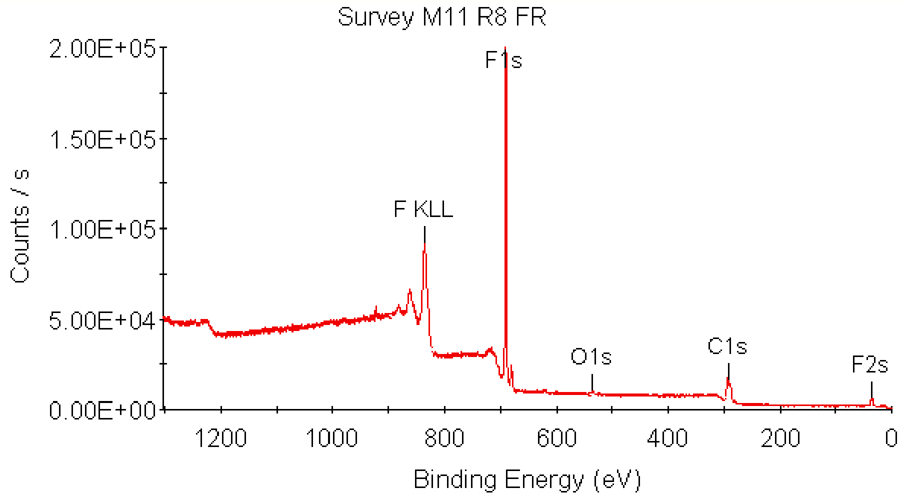
Plasma Finish retains desirable properties while allowing best quality solder joints

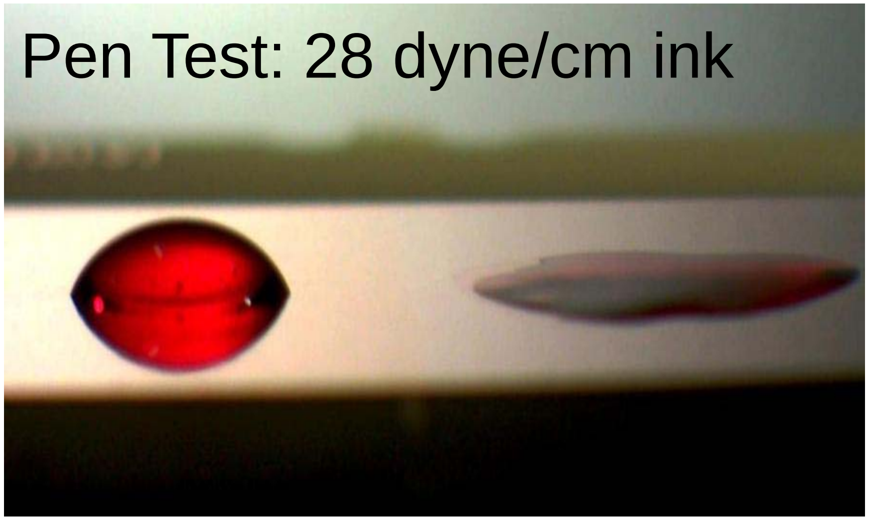
Fluoropolymer Properties

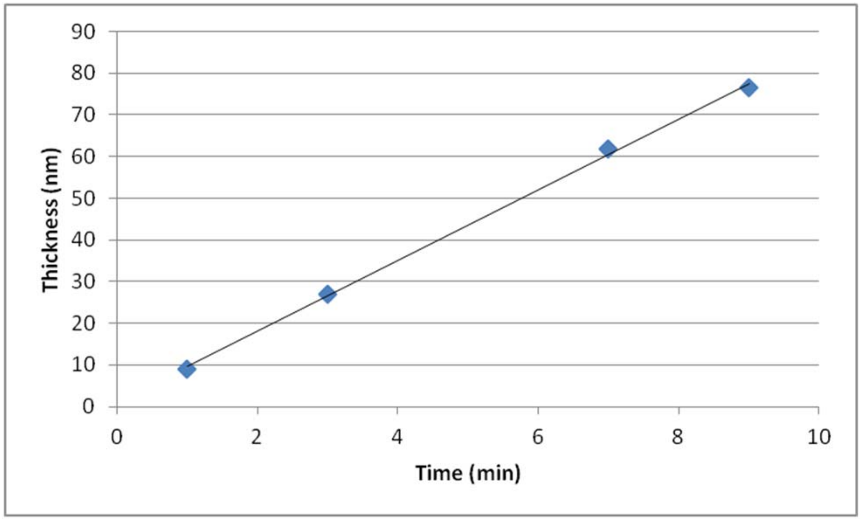


H$_2$O contact angle

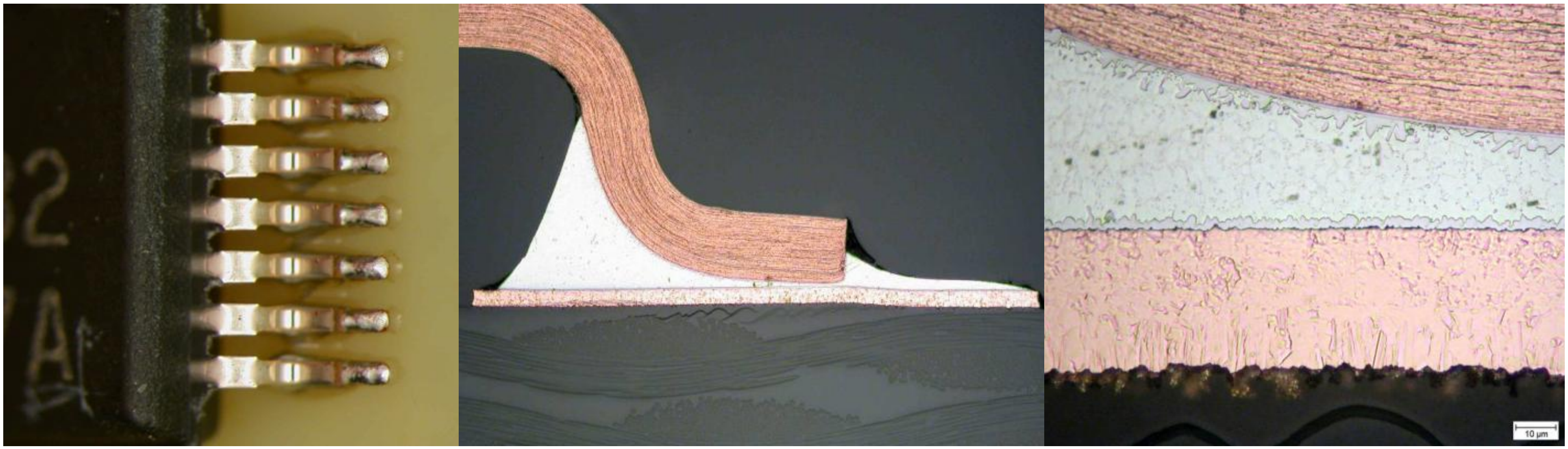








Solder Joint Characterization

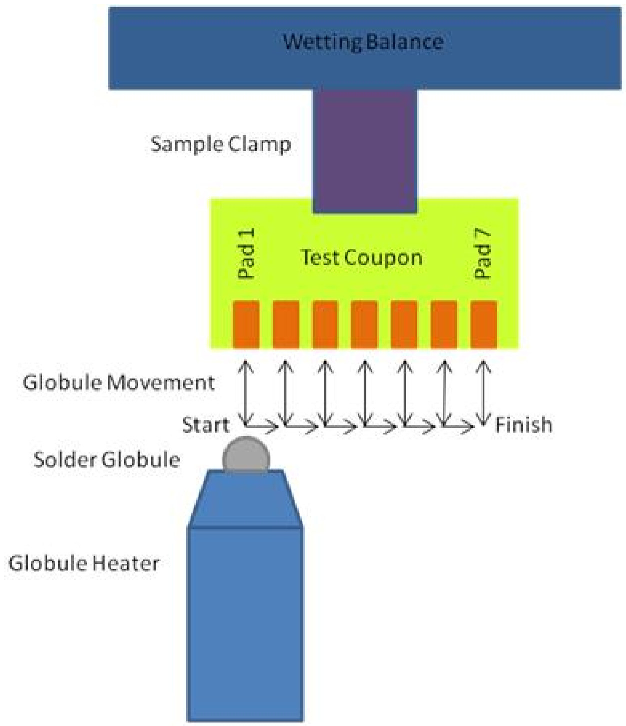


- Extensive testing carried out to prove reliability
- Accelerated aging, thermal cycling, shear testing, drop shock, etc

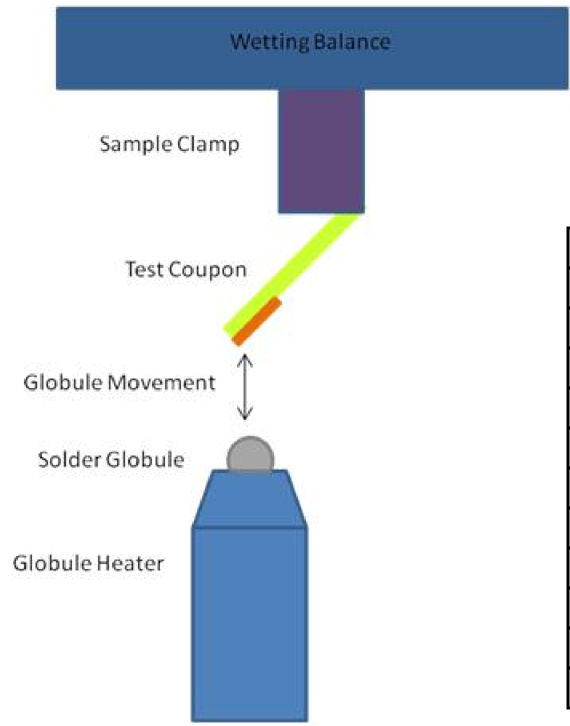
Fluoropolymer Solderability

- Wetting balance test set-up
  - MUST II+ wetting balance system (at The Welding Institute UK)
  - Each wetting balance test consists of testing the 7 pads on the test coupon individually using a 200mg solder globule.
  - The globule was fluxed in between each pad tested and the globule was replaced in between each coupon tested.
  - Materials for these tests were supplied by Gen3 Systems Limited (UK).
- The Pass/Fail criteria generally accepted as a benchmark and used by National Physical Laboratory (UK) are:
  - Force at time 2 s > 0.2 mN/mm (1.9 x 0.2 = 0.38 mN)
  - Time to 2/3 of Fmax in < 2 s
- These criteria are more rigorous than the IPC classification specifications laid out in the standard Solderability Test for Printed Boards IPC J-STD-003B.

Wetting balance test configuration



Front View



Side view

Test parameters

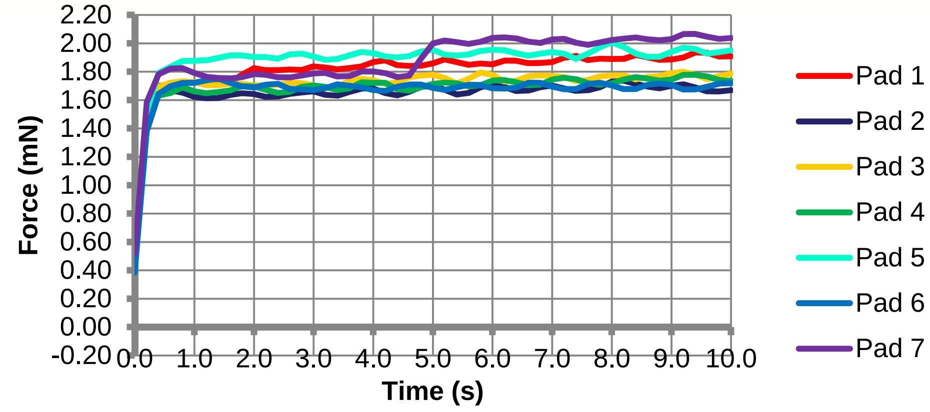
Pads	7
Pad size	1.9 x 3.7mm
Pad spacing	4.00 mm
Immersion depth	0.10 mm
Immersion Speed	1.0 mm/s
Flux	ACTIEC5
Solder	SAC305
Globule	200 mg
Receptacle	Globule 2
Wetting angle	45 deg
F1 Time	2.0 s
F2 Time	5.0 s

Solderability

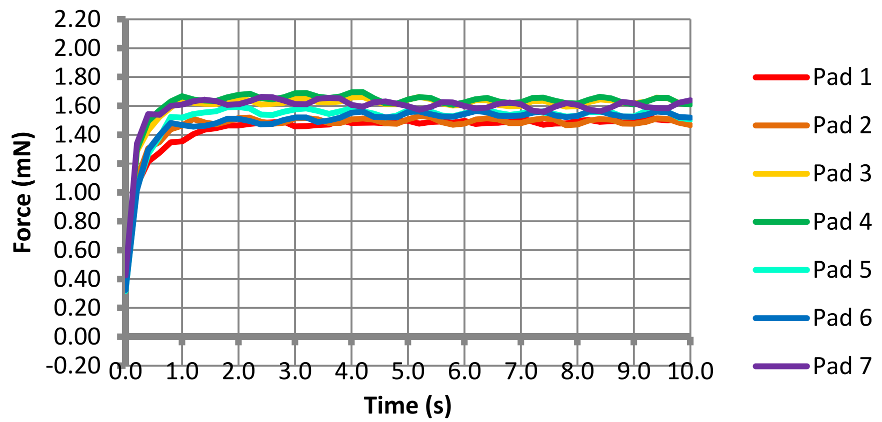
Test Parameters

Solder	SAC 305
Solder Temp (degC)	255
Flux	Actiec5
Imm. Speed (mm/s)	0.1
imm. Depth (mm)	0.1
Imm. Time (s)	10

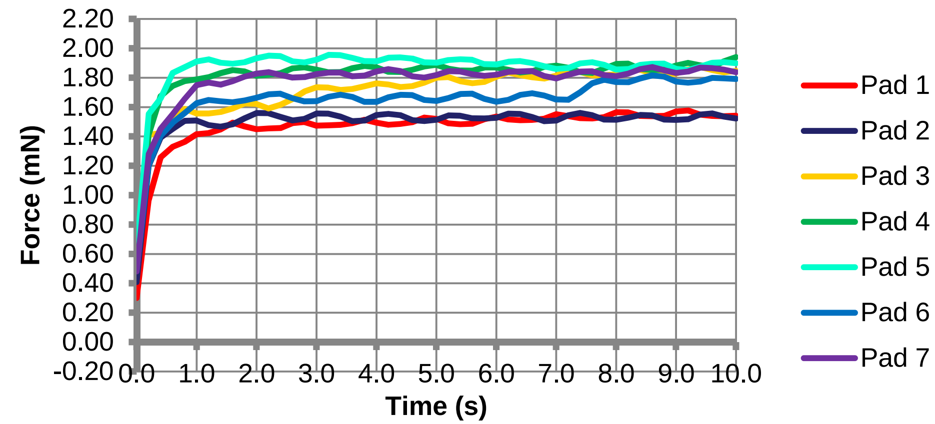
ImAg reference sample



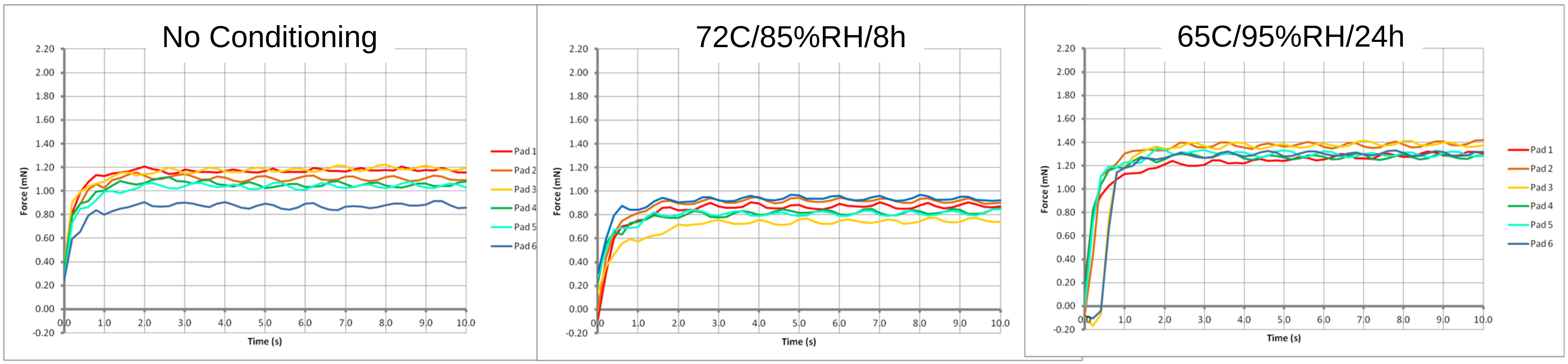
Fluoropolymer on Cu



Fluoropolymer on ImAg

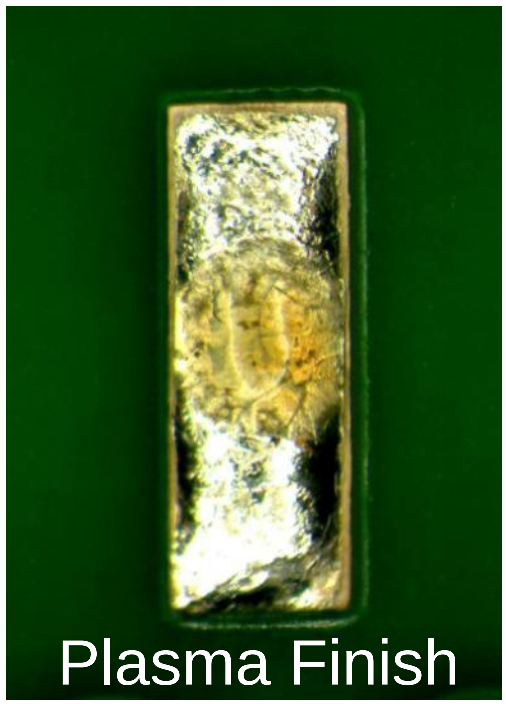


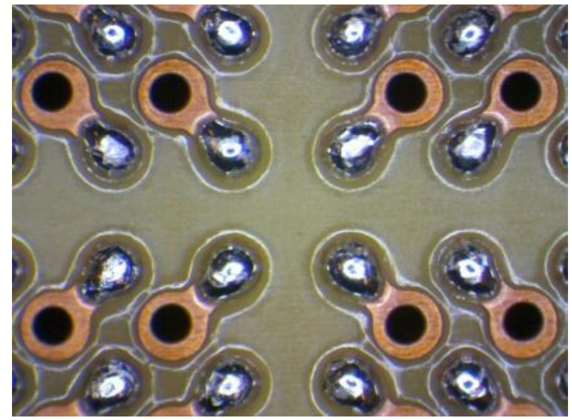
Fluoropolymer / ImAg Solderability



- Accelerated aging / shelf life conditioning
  - IPC J-STD-003B: 72C / 85 %RH / 8hrs (>6 months)
  - OSP test: 65C / 95%RH / 24Hrs (12 months)
- Slight or no change in wetting time
- Samples show good wetting even after these aggressive storage conditions

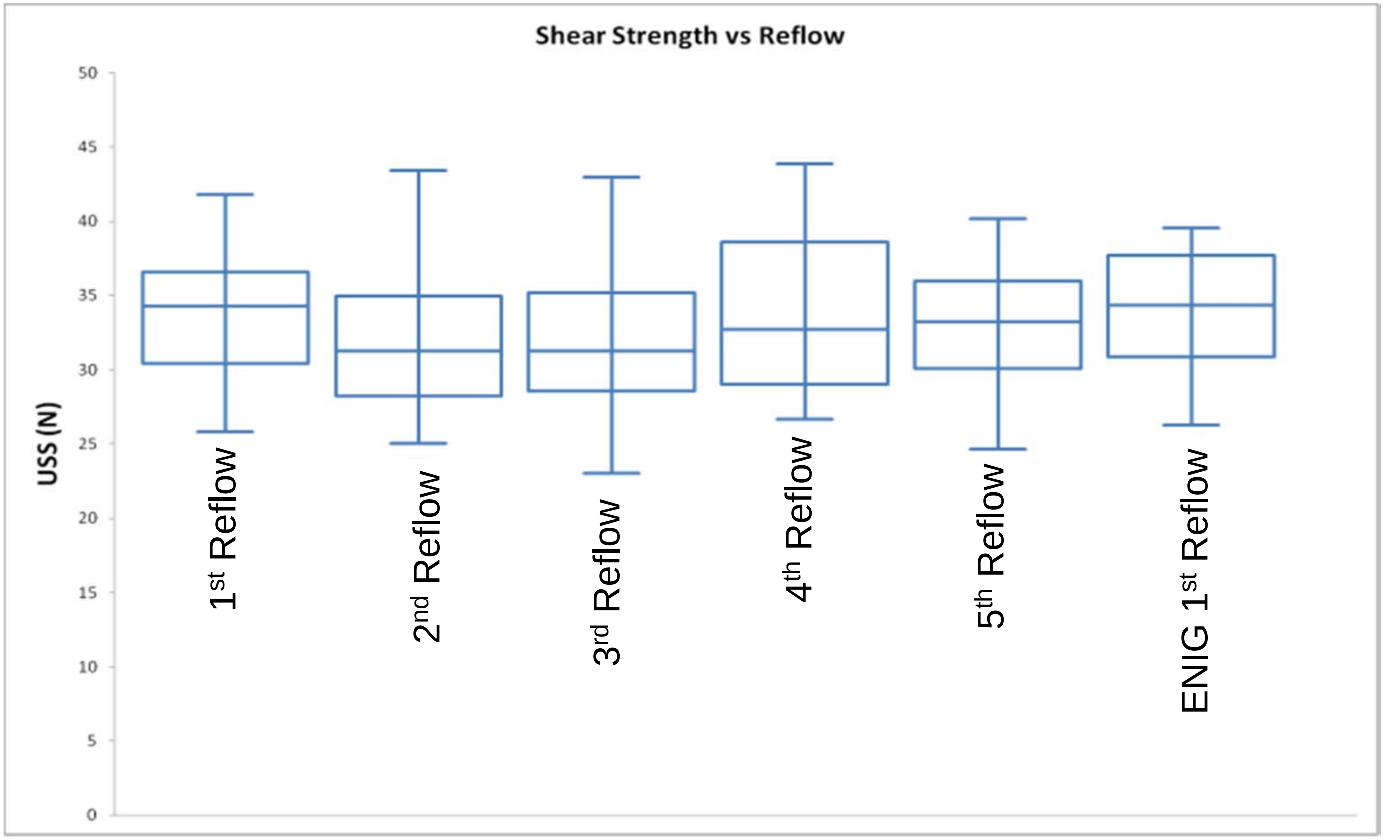
Flux Residue





- Hydrophobic nature of the fluoropolymer coating prevents flux from spreading along surface

Solder Joint Reliability



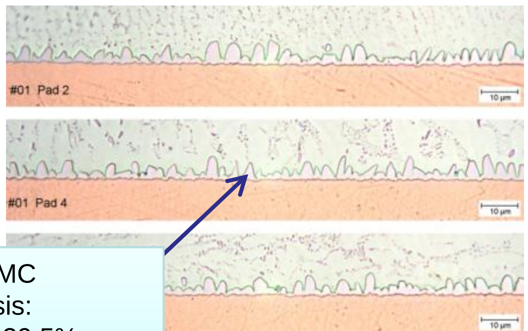
- Multiple reflows have no impact on shear strength

APEX EXPO 2012 IPC

Thermal Aging

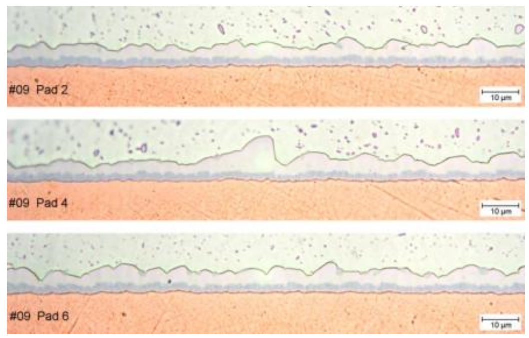
1000hrs at 150C

Cross Section OM 1000x of Solder Copper Interface (Quantum MicroMet)

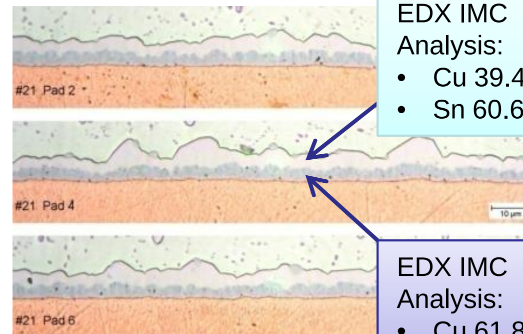


EDX IMC Analysis:
- Cu 39.5%
- Sn 60.5%

0 Hours



400 Hours

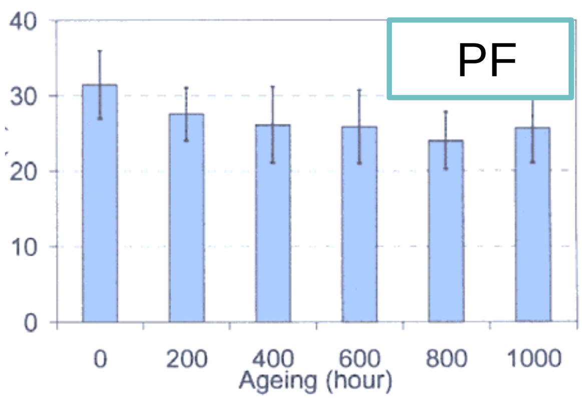


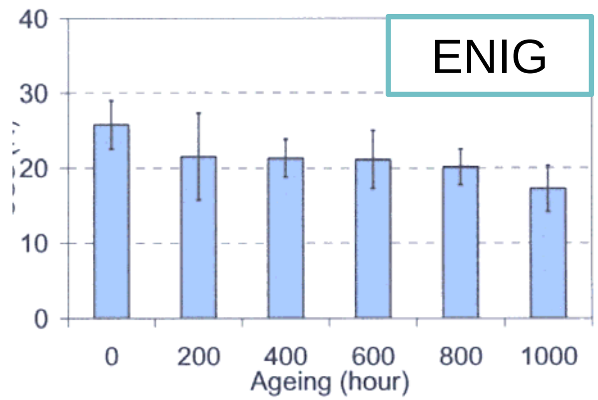
EDX IMC Analysis:
- Cu 39.4%
- Sn 60.6%

EDX IMC Analysis:
- Cu 61.8%
- Sn 31.2%

1000 Hours

Ultimate Shear Strength Test on R0603 resistors





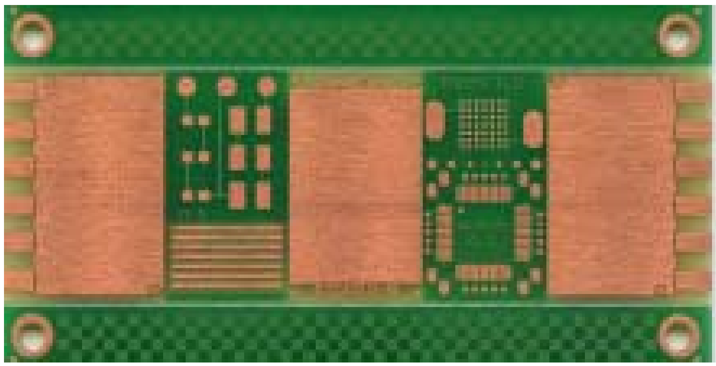
Plasma finish shows typical thermal aging and IMC growth behavior

Corrosion Testing

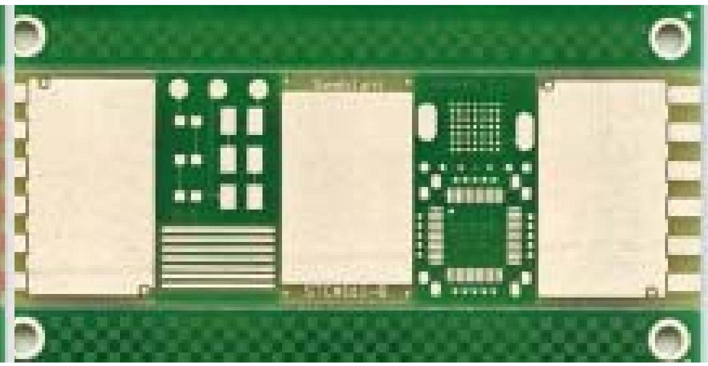
- Gas Phase SO_2
- Tire Factory Simulation
- Mixed Flowing Gas
- Chavant Clay

Gas Phase SO_2

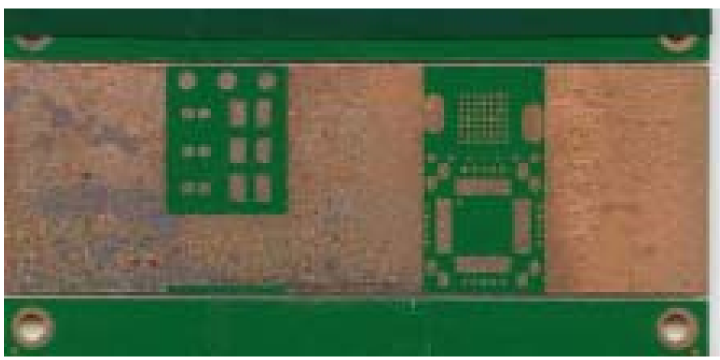
10ppm $S0_2$, 41.5^{o}C, >80% RH, 24 hrs



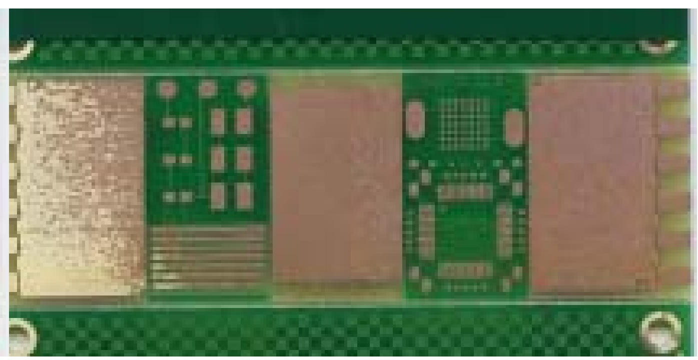
Cu + Plasma Finish



ImAg + Plasma Finish



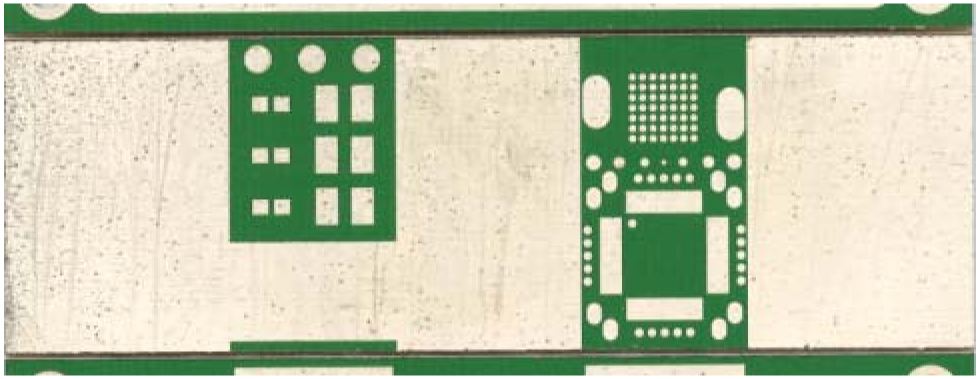
OSP



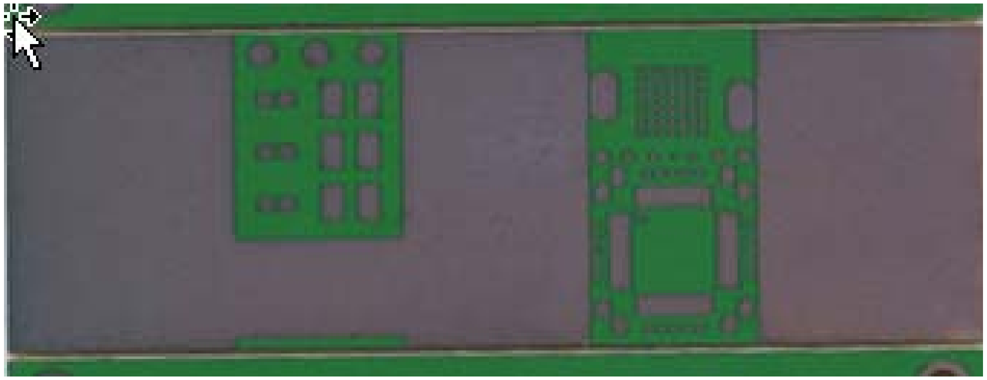
ImAg

Tire Factory Simulation

>95% Humidity at 50^{o}C for 22 hours, RT for 2 hours
24 hour cycle repeated for 1 week



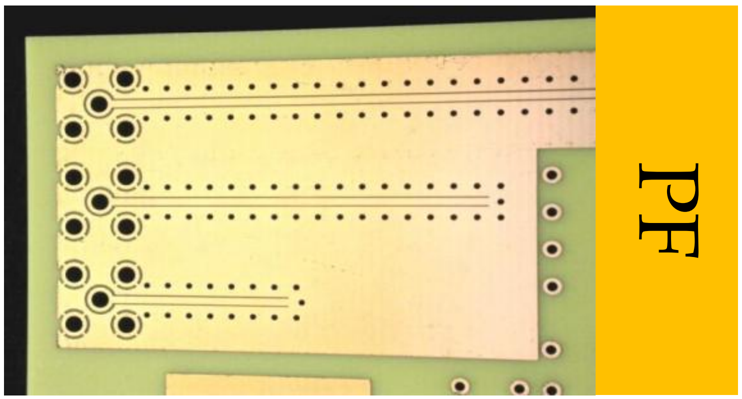
ImAg + Plasma Finish

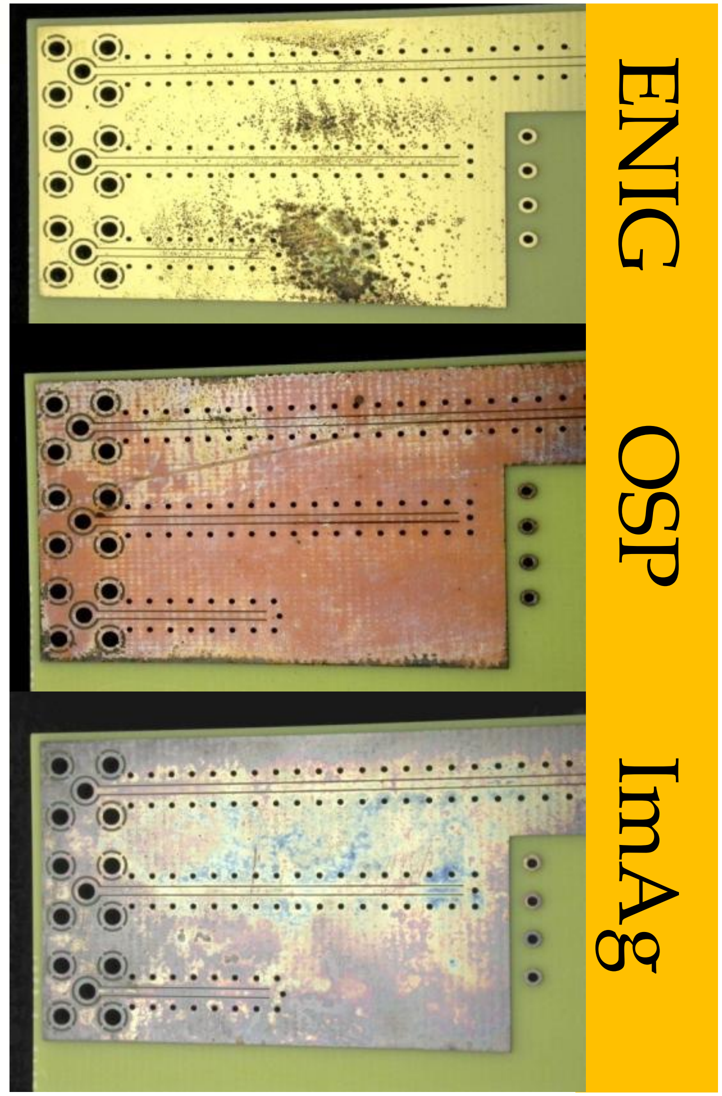


ImAg

Mixed Flowing Gas: Univ. of Limerick Stokes Institute

° C	% RH	Days	H_2S	SO_2	NO_2	Cl_2
30	70	20	100 ppb	200 ppb	200 ppb	20 ppb





% Surface Corrosion

Exposure Time (days)	ENIG	OSP	ImAg	PF
5	4	9	90	0
10	10	17	100	0
15	25	33	100	1
20	30	44	100	3

Plasma finish still acceptable at simulated 20 year life

Creep Corrosion Experiment

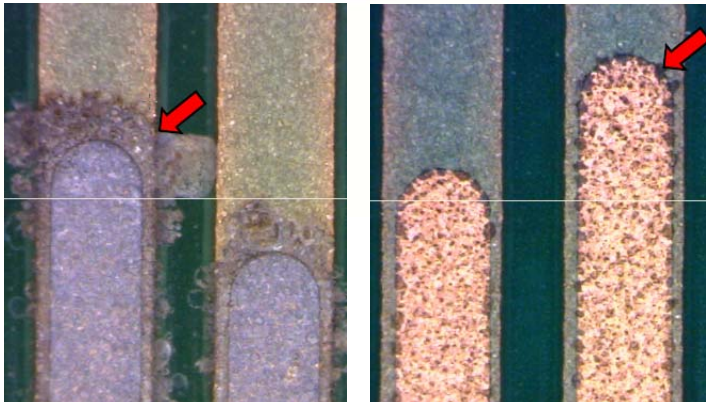
- Bare Cu, ImAg and Hi-P ENIG test vehicles manufactured by board shop
- 40nm fluoropolymer coating applied using plasma deposition system
- Test vehicles subjected to Pb-free reflow
- Chavant Clay testing at DfR Solutions
- Samples returned for visual inspection

Creep corrosion testing

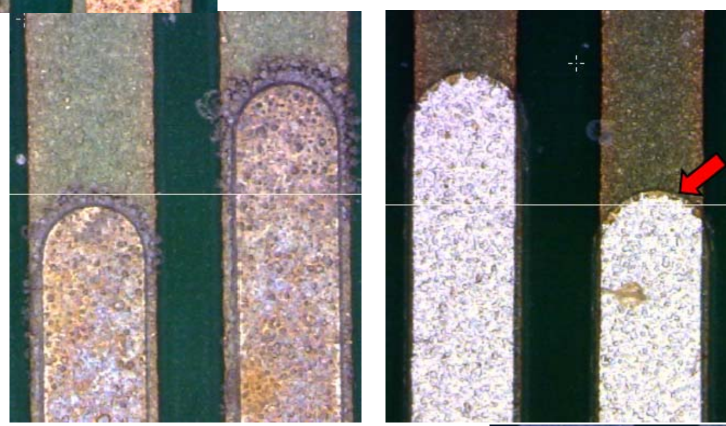
- Chavant clay test
  - Simulates clay modelling studio
  - Chavant J-525 sulphur bearing clay heated daily
  - Test samples at RT
  - Humid environment allows condensation

Testing performed at DfR Solutions

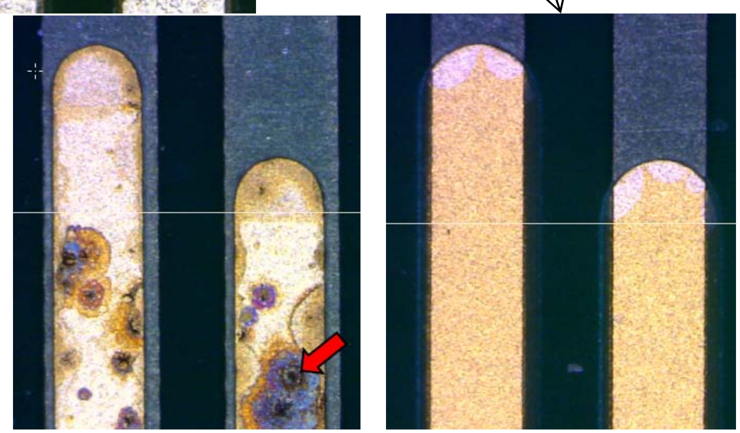
Chavant Clay Test



Cu



ImAg

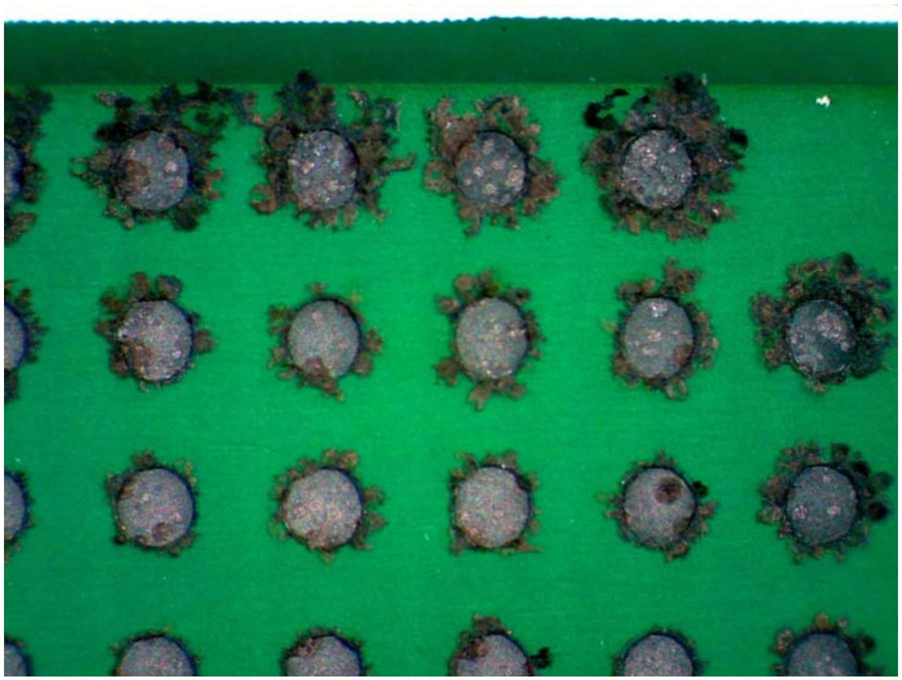


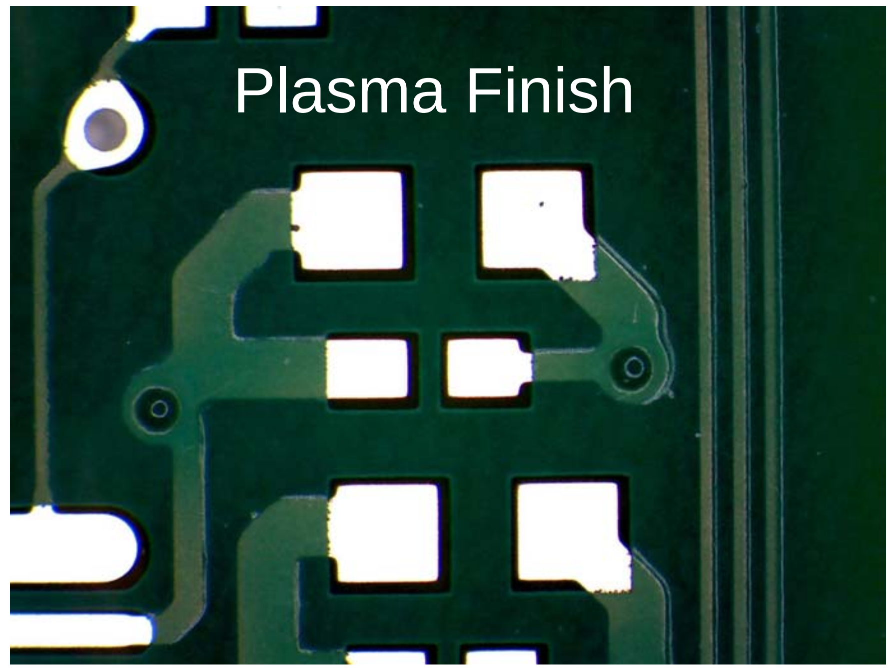
Hi P ENIG

Plasma Finish

Testing completed by DfR Solutions

Creep corrosion on ImAg





- Impact of Plasma Finish coating is clear

Conclusions

- Plasma deposited fluoropolymer allows for strong and reliable Pb-free solder joints
- Plasma finish can be used on copper as well as other surface finishes (i.e. ImAg, ENIG)
- The plasma finish increases shelf life and does not impede solderability
- Plasma coating acts as a significant deterrent to creep corrosion of PCBs in high sulphur environments

Acknowledgements

- Randy Schueller at DfR Solutions
- Nordson March
- Semblant R&D team

Thank You!

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