How Detrimental Production Concerns Related to Solder Mask Residues Can Be Countered by Simple Operational Adaptations

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ABSTRACT
The symbiotic relationship between solder masks and selective finishes is not new.

The soldermask application is one of the key considerations to ensure a successful application of a selective finish. The selective finish is the final chemical step of the PCB manufacturing process, this is when the panels are at their most valuable and are unfortunately not re-workable. Imperfections are not tolerated, even if they are wholly cosmetic. Quality issues often manifest themselves in the form of a 'ping pong' conversation between the fabricators, the soldermask suppliers and the selective finish suppliers. Without tangible evidence these discussions are difficult to resolve and the selective finish process is usually regarded as responsible.

Soldermasks identified as 'critical' in the field, and through testing, have been tested using state of the art technology to assess whether performance markers could be found.

This paper will focus on the chemical characteristics and use them to predict or identify potential issues before they occur rather than specifically name 'critical' soldermasks. It is also the intention of this paper to address the potential of a soldermask to react to common yield hiking practices like UV bumping and oven curing. It is hoped that this awareness will help fabricators to ensure maximum yields by asking the right questions.

'Critical' soldermasks impact all selective finishes. In this paper, practical experience using immersion tin will be used to highlight the relationship between 'critical' soldermasks and some of the issues seen in the field. The paper will include a novel approach to identify re-deposited volatiles after the reflow.

Key Words
Mass spectrometry
Soldermask
Extracted Ion Chromatogram
Ionic contamination

BACKGROUND
The function of a soldermask is to provide protection to the active circuit and definition for the selective finish. These fundamental attributes include photosensitivity for lithographic imaging and sufficient production environment resistance to protect the active circuit. These functions are simple in principle but the resultant implications can be far reaching. The impacts that will be focused on in this paper will be surface imperfections and where poignant, immersion tin will be used as an example.

The hazards of a 'critical' soldermask are primarily two fold (excluding developing residues): Leach out into process chemistries and solderability issues during multiple assembly steps.

Soldermasks were originally designed to facilitate Hot Air Solder Levelling (HASL). The need for co-planarity has seen the introduction of chemical selective finishes such as Electroless Nickel and Immersion Gold (ENIG), Electroless Nickel, Electroless Palladium and Immersion Gold (ENEPIG) and immersion tin to name a few. This change in application has obvious implications attached. Whereas HASL is a hot solder shock for 10 seconds, (approx. 260°C for eutectic solders and 280°C for lead free solders), the wet chemical selective finishes introduce longer dwell times in harsh chemical environments, often at high temperatures. In an ideal world, the selection of the solder mask would be optimally coupled with the selective finish employed. In the real world, however, the cost factor is prevalent as a selection tool. To counter this notion an attempt will be made in this paper to raise awareness of the components within a soldermask that render it potentially 'critical' to production.

It is equally perplexing that in this day of 'high tech' 6 sigma process control, the quality of the solder mask process is still judged by weight gain, Stouffer wedges, break point tests and the temperature of the baking ovens. Whilst all these controls ensure a good coating they provide no information on the status of curing or the potential for volatile release during selective finish processing or assembly.

It must be stressed at this stage, that soldermasks fulfill a fundamental part of circuit manufacture and that, in the main, this is achieved very successfully. The virtual eradication of soldermask residues after developing is testament to the advancement in the imaging arena. For this paper we will assume that resist residues have been totally eradicated and focus on the impact of leaching. Leaching of the soldermask into the chemistry has been shown to have lifetime and quality impacts. This is true of all the mainstream selective finishes.

This paper will identify soldermask constituents that can be 'critical' to production through the use of state of the art analysis equipment and demonstrate that traditional industry fixes such as UV bumping, if adopted, have little impact on eradicating the potential risks to yield. The soldermasks selected as 'critical' are based on field experience.

THE IDENTIFICATION OF POTENTIALLY PROCESS 'CRITICAL' COMPOUNDS IN SOLDERMASKS

Methodology

For the purpose of this investigation 8 samples were selected based on field experience and 4 samples are taken from 'critical' customer panels and are identified as A, B, C and D. These are described in Table 1.

Table 1: A description of the test population

Sample ID	Description	'critical' Y/N
1	FR4 (Reference)	N/A
2	Light Green, Gloss	N
3	Dark Green, Gloss	Y
4	Black, Matt	N
5	Dark Blue, Gloss	N
6	Black, Matt	Y
7	Grey/Black, Matt	N
8	Green, Matt	Y
A	Customer	Y
B	Customer	Y
C	Customer	Y
D	Customer	Y

The analysis methods employed, as listed in Figure 1 are:

- Elemental analysis (CHNS) – Quantification method for the chemical composition of carbon, hydrogen, nitrogen and sulphur
- Fourier Transform Infrared spectroscopy (FTIR) – A finger print/ Identification of functional groups.
- Leaching experiments – Extracts were analyzed by GC-MS and HPLC-MS – Identification of leach out products.
- Pyrolysis – GC-MS – Identification of high molecular weight compounds

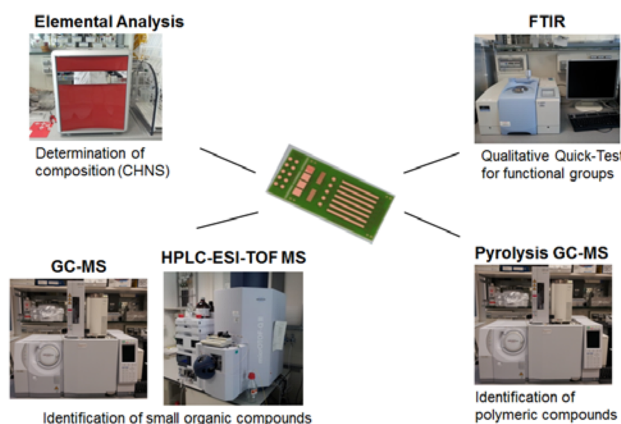


Figure 1: demonstrates the state of the art analysis applied

Elemental Analysis

This is a destructive technique that identifies the basic chemical characteristics by quantatively isolating the elements carbon, hydrogen, nitrogen and Sulphur (CHNS). This method examines the properties of the soldermask but can only be used as an early indicator. Although it is apparent that there is a discrepancy between the ‘critical’ and non-’critical’ soldermasks, this method cannot determine the impact of this discrepancy on the plating processes.

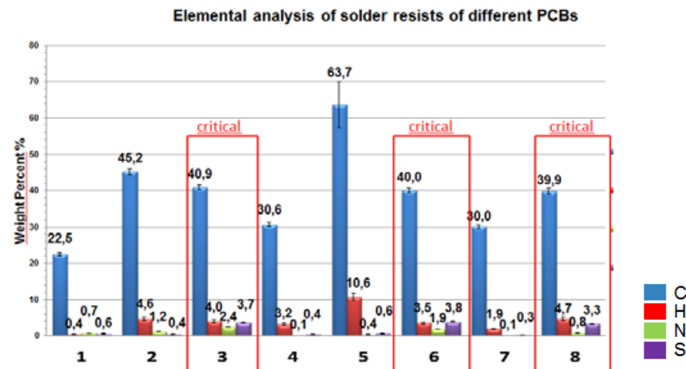


Figure 2: The elemental analysis of the test population

Figure 2 indicates that the presence of sulphur is the key difference between the ‘critical’ and non-’critical’ soldermasks. This is better demonstrated in Figure 3 in which only the Sulphur content is mapped.

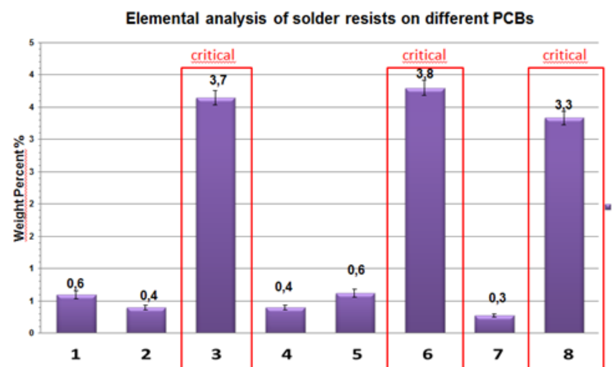


Figure 3: The elemental analysis of the test population focusing on the Sulphur content

Whilst there is most likely a rational explanation for the presence of sulphur, the question that should be considered is whether weight percentages over 3 are required and whether an alternative exits. This is beyond the expertise of our facility and as such will not be further extrapolated upon.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a non-destructive technique that could be applied on site. It is a quick test requiring no preparation resulting in a wavenumber according to the molecules ability to absorb infrared light. This method can be used to identify the functional groups. Figure 5 demonstrates that at wave numbers of between 1075 and 1077 cm^{-1} a signal can be observed for the ‘critical’ sample. From the elemental analysis it has already been established that sample ID 3 has a sulphur weight percentage of 3.7%. The wavenumber at 1075 cm^{-}1 probably indicates the presence of sulphur. This method also indicates a discrepancy between the ‘critical’ and non-’critical’ soldermask. Due to the complexity of the soldermask chemistry, this method maybe used as a finger printing technique to direct further analysis.

Figure 4: Comparison of 'critical' soldermask to non-'critical' and reference

Figure 4 compares a cross-section of the population whilst figure 5 focusses on the comparison of the 'critical' population members. It can be demonstrated that the 'critical' soldermasks exhibit similar absorption signals at the almost the same wavenumbers.

Figure 5: Similarities of all 'critical' soldermasks

This method has the potential to be a performance indicator.

Leaching Experiments

This is a simulation of the potential of a soldermask to leach into the plating chemistry. Acetonitrile, (ACN), is used as a solvent. The samples are exposed to the solvent to extract the potential leachants. The resulting extracts were analyzed by GC-MS and HPLC-ESI-TOF MS. In this work only the results of the HPLC-ESI-TOF MS are shown. Therefore the compounds of the extracts were separated by liquid chromatography and analyzed by mass spectrometry. The resulting high resolution mass spectra were used for the calculation of sum formula, which allows a prediction of structures which can be compared with reference substances. Hence, it is possible to identify additives like photo-initiators, cross-linkers, flame retardants and other plastic additives. Figure 6 and Figure 7 show the comparison of the signals of the photo-initiators. For a better comparison, the Extracted Ion Chromatograms are used. Therefore the desired mass was extracted from the whole mass spectrometric data. In comparison the samples show differences in their signal intensities of photo-initiators. It should be noted that the identified photo-initiators contain sulphur. The following table demonstrates the correlation between sulphur in the elemental analysis and the response of the mass signals. In general, samples with high sulphur content show intense signals of leaching products. This is especially true for the sulphur containing photo-initiators and is demonstrated in Figures 6 and 7.

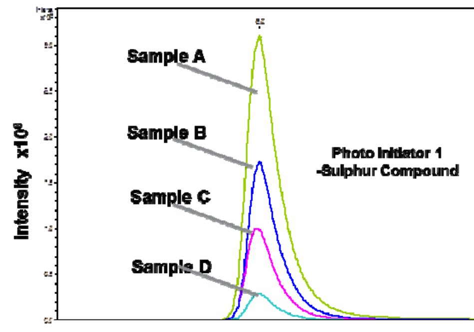


Figure 6: Extracted Ion Chromatogram of Photo Initiator 1

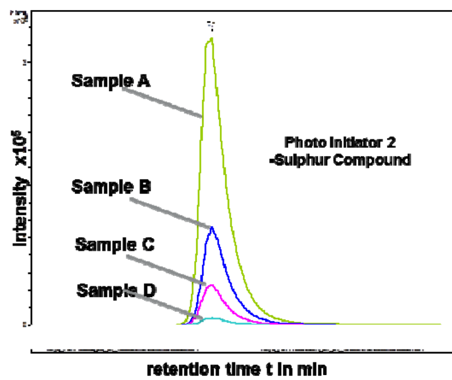


Figure 7: Extracted Ion Chromatogram of Photo Initiator 2

Table 2: Elemental analysis of ‘critical’ customer samples A, B, C and D

Sample	S (ea)
A	6.4%
B	3.3%
C	2.8%
D	2.7%

Figures 6, 7 and 8 demonstrate the correlation between sulphur in the elemental analysis and the response of the extracted ion chromatogram.

Pyrolysis and GC-MS

A sample of less than 200µg is scraped from the material to be examined. This is then exposed to temperatures of 550°C. The impact of this is to fragment the molecules. The fragmented molecules are then separated by gas chromatography and subsequently identified by mass spectrometry. This method can be used to identify the polymeric compounds of soldermask. Due to the sensitive nature of the industry response charts will not be included in this paper as they may infringe upon confidential know how. The take away message, however, is that whilst the signal responses for ‘critical’ soldermasks are similar they differ from those of non-’critical’ soldermasks.

THE IMPACT OF TRADITIONAL YIELD HIKING TRICKS ON ‘CRITICAL’ SOLDERMASKS

A typical ‘trick’ within the industry to increase yields is to use ultraviolet (UV) bumping. This is a pre-selective finish treatment aimed to completely ‘harden’ or polymerize the soldermask and prevent release of volatiles during the selective finish process or reflow process.

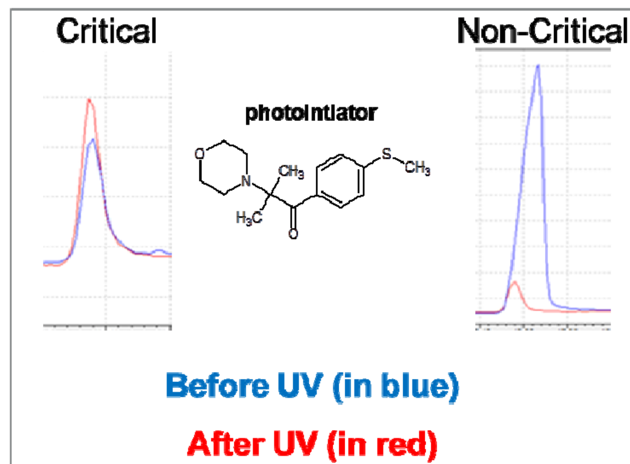


Figure 9: GC-MS results for 'critical and non-critical solder masks before and after UV bumping.

Figure 9 demonstrates that the signal is the same for the critical soldermask before and after >UV bumping. This an indication that the soldermask is not polymerized or that there is too much photo-initiator in the soldermask matrix.

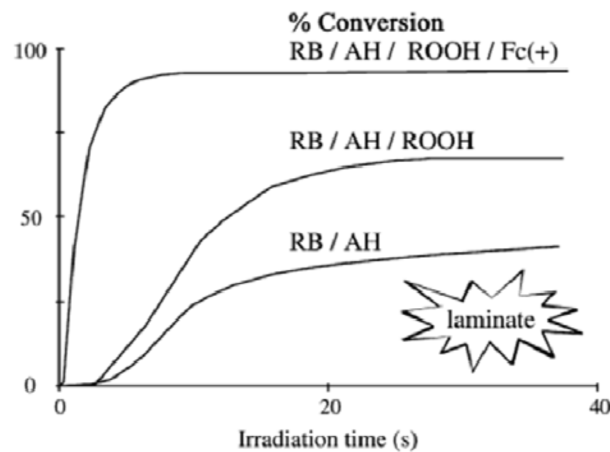


Figure 10: A representation of polymerization [1]

Figure 10[1] demonstrates that % conversion (polymerization) is related to irradiation time. The labels on the curves refer to 3 different monomer systems. The best situation is full polymerization in a short irradiation time(s). The Figure also demonstrates that it is possible that full polymerization can never be achieved. This is usually the case if there is too much photo-initiator in the matrix.

This excess of photo-initiators has the potential to result in outgassing volatiles during reflow.

RELATING THEORY TO REALITY

In practice, critical solder mask types can be potentially responsible for soldering issues. To demonstrate this, a test was performed at a PCB facility. Four soldermask types were used in the test and the post soldermask bake was varied in terms of time, and the UV energy for the solder bump was varied (refer to the test matrix in Table 3).

Table 3: Test Matrix

solder mask type	Post Cure @ 150°C (min)	UV energy (mj/cm²)
A, B, C & D	60	0
		1500
		2000
		2500
		3000
A, B, C & D	90	0
		1500
		2000
		2500
		3000

The outputs from Table 3 are an evaluation of the solderability in the form of a solder gap test and a measure of the ionic contamination which can be correlated to the volatiles within the soldermask.

Figure 11 is verification that the ionic contamination is a viable representation of soldermask polymerization. The evidence for the soldermask being the dominant cause of ionic contamination is proven by the result for the sample without soldermask, (the column marked as 'no SM'). As a point of interest, soldermask C also displays low values suggesting complete polymerization.

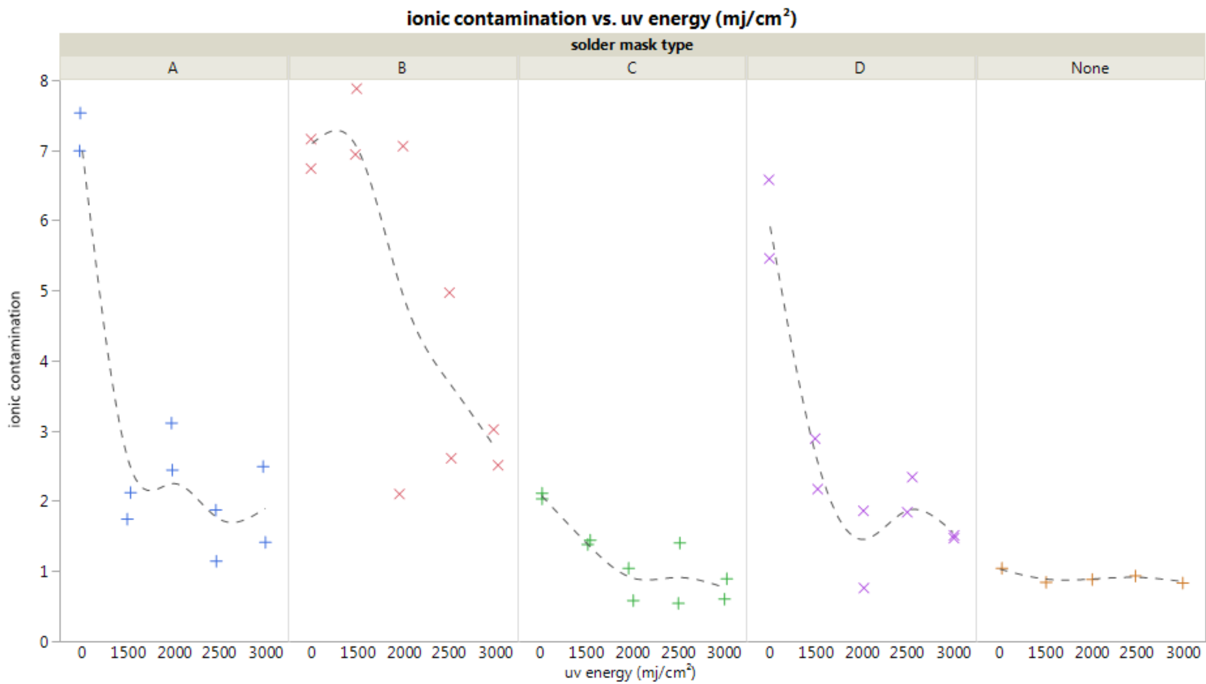


Figure 11: The relationship between soldermask, UV energy, and ionic contamination

To evaluate solderability, a test vehicle was selected that simulates wettability. The test vehicle is tool generated by the chemical supplier responsible for the data generated for this paper. The coupon is shown in Figure 12.

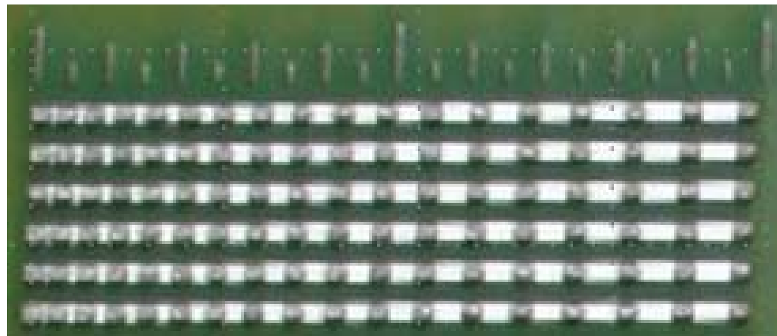


Figure 12: Solder spread test vehicle

The mechanism of the test is to print solder paste in a pattern whereby the gap between solder paste deposits increases. When the samples are reflowed, the solder paste will spread to represent solderability.

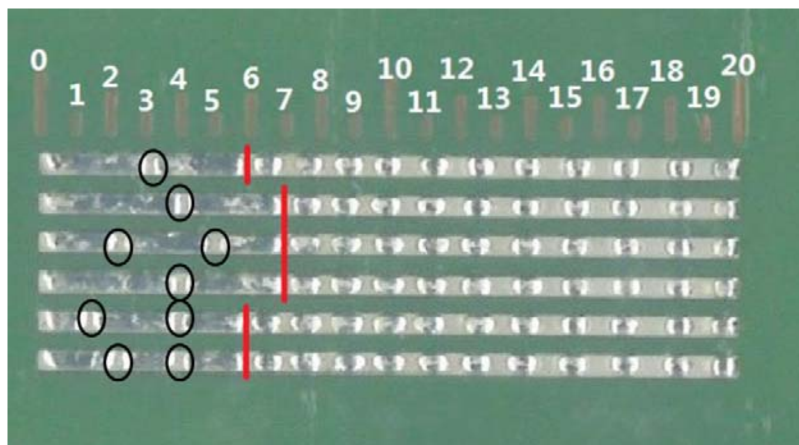
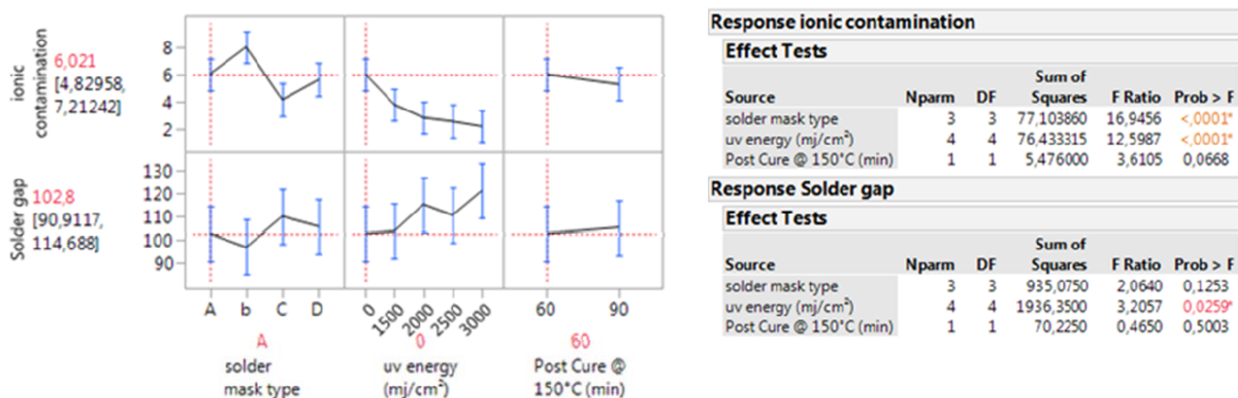


Figure 13: Solder spread test vehicle after reflow

The test vehicle is a tool that can provide a numerical value. The value is calculated by summing up the maximum spread values, (red line) and subtracting the number of breaks, (black rings) divided by 2. Therefore the result for figure 13 is (6+7+7+7+6+6) – 9/2 = 35.

These values were used to evaluate the impact of simple techniques to enhance production yields.



Response ionic contamination

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
solder mask type	3	3	77,103860	16,9456	<,0001*
uv energy (mj/cm²)	4	4	76,433315	12,5987	<,0001*
Post Cure @ 150°C (min)	1	1	5,476000	3,6105	0,0668

Response Solder gap

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
solder mask type	3	3	935,0750	2,0640	0,1253
uv energy (mj/cm²)	4	4	1936,3500	3,2057	0,0259*
Post Cure @ 150°C (min)	1	1	70,2250	0,4650	0,5003

Figure 14: The results and significance for ionic contamination and solderability

The results show that the ionic contamination is statistically related to the solder mask type and UV energy. It must be stressed that the UV energy is not a setting recommendation, as the measuring techniques and equipment can give significantly varied results, but just to indicate more energy or less energy.

In this test, more UV energy reduces ionic contamination and the impact of the UV energy is also statistically significant for with regards to the solder gap test. In other words, a UV treatment prior to the i-Sn plating process, significantly improves ionic contamination and soldering behavior.

CONCLUSIONS

The primary finding of this paper was that sulphur (>3%) can be found in solder masks that were identified as 'critical' and could therefore be used as a marker to highlight them.

The samples tested were supplied from the field and do not represent any supplier specifically. As previously mentioned it is the intention of this paper to help educate users to ask the correct questions about the solder mask they are using. Whilst UV treatment prior to plating is effective, it can be seen that selecting a suitable solder mask can also impact yield. In the customer based test, solder mask C had the lowest ionic contamination results and the best solderability results.

In addition, further study would be necessary to identify the true mechanisms involved. Although the ionic contamination has been demonstrated to be inversely related to the application of UV energy, it is unclear whether source of the ionic contamination can be attributed to the soldermask or the plating solution. It would be acceptable to hypothesize that the increase of SM polymerization simply reduces the absorption of chemistry. Ionic contamination can also be measured for the sample without soldermask in figure 11.

REFERENCES

[1] J.P.Fouassier, X.Allonas, D. Burget, Photopolymerization reactions under visible lights: principle, mechanisms and examples of applications, Progress in Organic Coatings, 47 (2003), 16-36.