IS IT POSSIBLE TO USE MARKERS TO SELECT THE RIGHT SOLDERMASK TO OPTIMIZE THE YIELD OF YOUR SELECTIVE FINISH?

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ABSTRACT

The symbiotic relationship between soldermasks 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 article to address the potential of a soldermask to react to common yield hiking practices like UV bumping. 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 article immersion tin will used to highlight the relationship between ‘critical’ soldermasks and some of the issues seen in the field. The article will conclude with a novel approach to identify re-deposited volatiles post reflow.

Key Words

Mass spectrometry
Soldermask
Extracted Ion Chromatogram

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 article 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.

Figure 1: Potential Failures due to ‘‘critical’’ Soldermasks REF immersion Tin

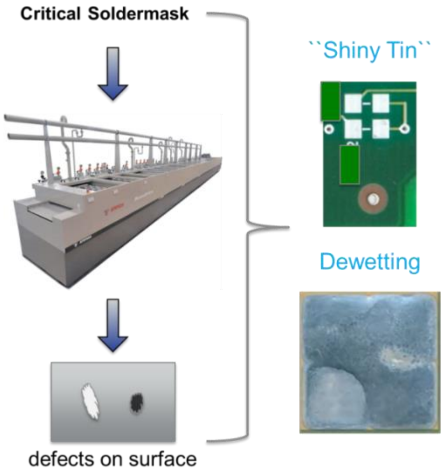


Figure 1 only highlights the issues due to leach out into the active solutions. A ‘critical’ soldermask can also have detrimental impact on the assembly processes such as reflow, as previously mentioned.

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 ENIG, 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 article 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 article 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 article 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 form ‘critical’ customer panels and are identified as A, B, C and D. These are described in Figure 1.

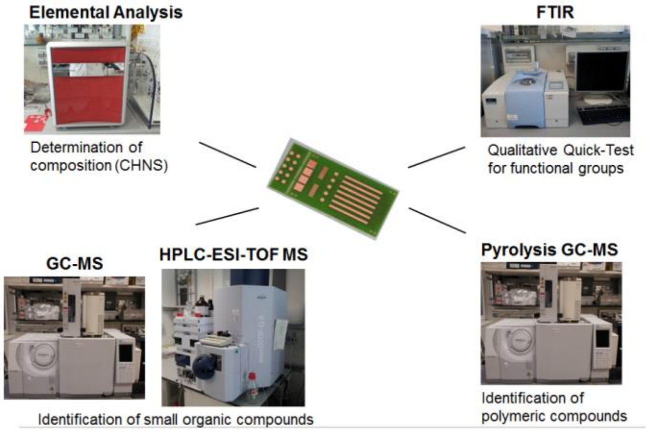
Figure 1: A description of the test population

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 2 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 2: 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 3: The elemental analysis of the test population

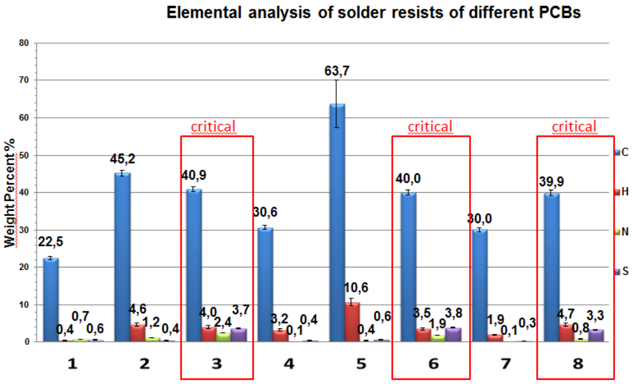
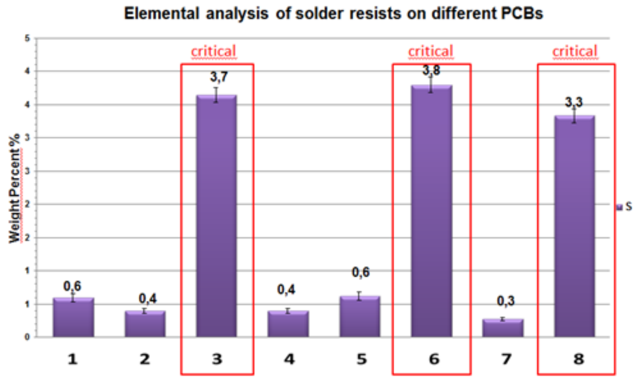


Figure 3 indicates that the presence of sulphur is the key difference between the 'critical' and non-'critical' soldermasks. This is better demonstrated in Figure 4.

Figure 4: 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 5: Comparison of 'critical' soldermask to non-'critical' and reference

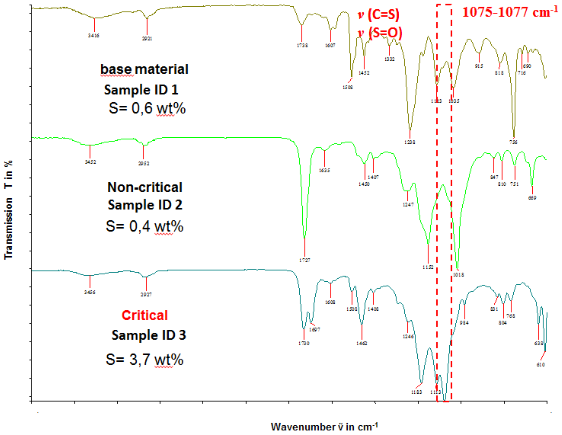
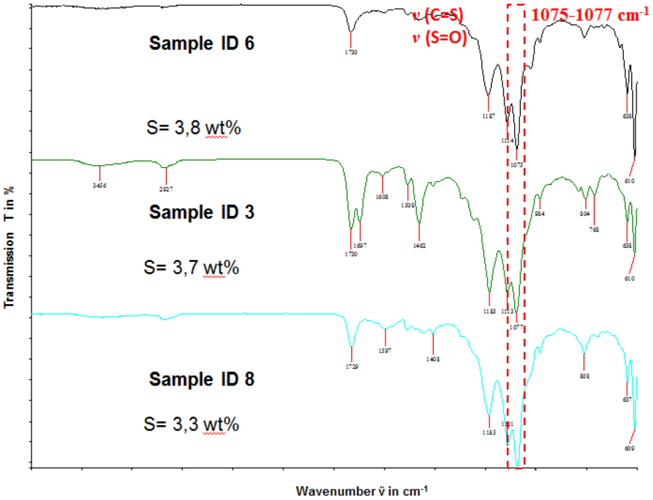


Figure 5 compares a cross-section of the population whilst figure 6 focusses on the comparison of the 'critical' population members. It can be demonstrated that the 'critical' soldermasks exhibit similar absorption signals at the almost the same wavenumbers.

Figure 6: 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 7 and figure 8 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 a high sulphur content show intense signals of leaching out products. Especially the sulphur containing photo-initiators. This is demonstrated in Figure 7 and 8.

Figure 7: Extracted Ion Chromatogram of Photo Initiator 1

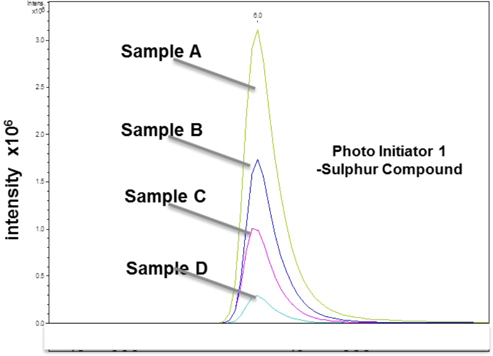


Figure 8: Extracted Ion Chromatogram of Photo Initiator 2

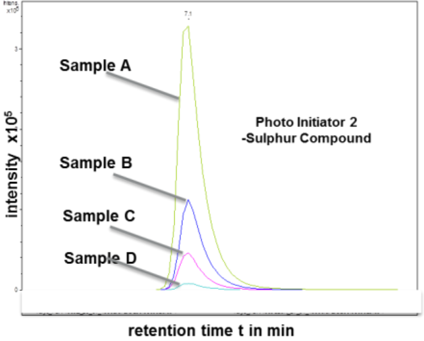


Figure 9: Elemental analysis of 'critical' customer samples A, B, C and D

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

Figures 7, 8 and 9 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 article 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.

It has been demonstrated that high sulphur content (>3%) identified by the elemental analysis can be correlated to, (used an indicator), more accurate analysis methods to indicate an increased presence of photo-initiators.

Figure 10: GC-MS results for 'critical and non-critical solder masks before and after UV bumping.

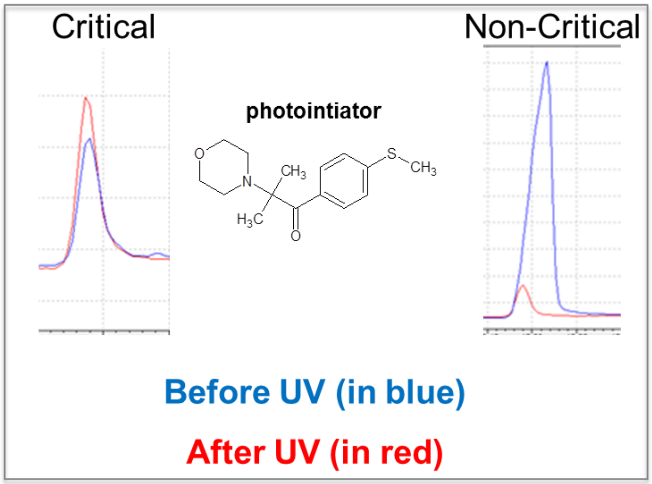


Figure 10 demonstrates that the signal is the same for the critical soldermask before and after >UV bumping. This an indication that the soldermask is not polymerized or that there is too much photo-initiator in the soldermask matrix.

Figure 11: A representation of polymerization

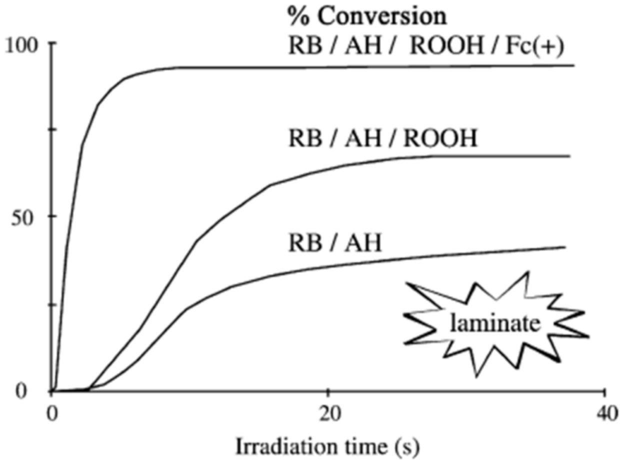


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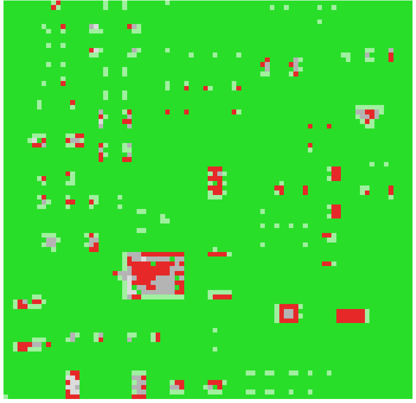
Figure 11[1] demonstrates that polymerization can only be improved if the initial irradiation ended early. The best situation is full polymerization in a short irradiation time (s). The figure also demonstrates that it is possible that full polymerization can never be achieved. This is usually the case if there is too much photo-initiator in the matrix.

This excess of photo-initiators can result in volatiles during reflow.

IDENTIFICATION OF REDEPOSITED VOLATILES POST RE-FLOW

One of the main advantages of metallic selective finishes is the ability to perform multiple reflow cycles. Although, the finishes are robust, 'critical' soldermasks can release volatiles during the first reflow cycle that redeposit on the backside of the panel. This is especially true of lead free solders that require a nitrogen environment under vacuum, resulting in no extraction. This is a prime example of a failure that can lead to discussions between suppliers and fabricators. Atotech is developing a novel method to identify these residues. At this stage the approach is in it's infancy and as such will not be elaborated on further than to show some tantalizing evidence.

Figure 13: A Novel Approach to Identifying Residues Post Reflow (Critical Soldermask)



The areas in red are residues that cannot be seen by the naked eye or identified by EDX. EDX analysis usually cannot detect thin residual films as the background interference is too high.

The image in figure 13 is simply a demonstration of the potential for this novel approach to identify residues post-reflow. This technique can be used to select soldermasks that do not release volatiles during reflow and may provide an alternative tool to EDX.

CONCLUSION

This article demonstrates that analysis can yield markers to identify 'critical' soldermasks.

The primary finding of this study was that sulphur (>3%) can be found in soldermasks that were identified as 'critical'. It is also accepted that further work is required to firmly link 'critical' soldermasks to quality issues. This means turning on the problem. This topic is being discussed as we are aware that our definition of 'critical' has come from experience in the field.

Further studies will include optimizing the leaching solution to truly reflect the process matrices and times. The tests outlined above were carried using solvents and times that do not reflect the true processes available.

The samples tested were supplied from the field and do not represent any supplier specifically. As previously mentioned it is the intention of this article to help educate users to ask the correct questions about the soldermask they are using. It can also be seen that selecting the correct soldermask maybe more effective than employing corrective actions like solder 'bumping'.

REFERENCES

[1]J.P.Fouassier, X.Allonas, D. Burget Photopolymerization reactions under visible lights: principle, mechanisms and examples of applications