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Influence of N_2 Atmosphere on the Contamination Effects of Lead-free Solder Paste During Reflow Soldering Processes

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Abstract

"Lead-free" concept introduction in electronics industry presents many challenges for all companies implied in the supply chain, and a key concern remains the non defined nor mastered impact on the soldering process itself. Lead-free alloys melting point is higher compared to the usual Pb based alloys used up to now, and this temperature increase means also a potential increase of the oxides formation, main enemy of stability and reliability of the final joints. One area posing a challenge is the flux performance. In the reflow process, fluxes with higher activity have been developed to offer an attractive alternative to oxides formation. Main drawback is the residue amounts that weaken mechanically the joint and increase corrosion sensibility.

The purpose of this study is to evaluate the possible influence of an inerting atmosphere on the residues formation during the reflow process.

Five lead-free solder pastes have been selected with various activity levels. Wetting forces and time measurements have been determined with the method developed by Air Liquide in 2002 and based on the Malcom SP2 device. This specific and high performance equipment allows simulating the temperature profile of a reflow process and has been adapted to work under controlled atmospheres. This test is then very representative of reflow soldering processes.

Results under air and N2 are compared. Some solder pastes present similar wettability behaviour between Air and Nitrogen : theses pastes are the most activated ones and by then are supposed to imply a higher residue level on the boards.
On this purpose, these measurements have been completed by residues characterization tests which now become an essential point with lead-free processes. The usual SIR test, IPC-TM-650 2.6.3.3, is widely used in industry but offers no challenge and is not representative of actual products, as specified in the SIR Handbook IPC-9201. The following tests have then been chosen:

- SIR based on standard IPC-TM-650 2.6.3.3 but with lower standoffs and a Ni-Au finish, that are closer to today's boards design
- and BONO test, used in France to characterize corrosion resistance, which is known to be more selective.

Main trend is that higher residues deposition effects on joint resistance can be recovered by inerting, and various effects of nitrogen are underlined, such as the significant decrease of the measurement dispersion. Nitrogen offers an alternative to higher activated fluxes and to contaminants effects.

Introduction

With the move toward lead-free introduction, the assembly industry has to face a new challenge, which is the increase of soldering temperatures and the associated increase of oxidation. To reduce these effects of oxidation and allow sufficient wetting, pastes formulations have been modified by solder pastes manufacturers.[1] Moreover, commercial and technical brochures generally indicate that solder pastes are developed to give good results with both air and nitrogen.

As the new formulations usually include more activated flux, they may raise some issues related to residue formation: whether those compounds have an effect on the reliability of the end-product will be discussed in this paper.

One alternative solution to the increase of temperature and oxidation, while keeping low activation pastes, is to inert reflow ovens. But the use of nitrogen represents an added cost and, by then, need to be fully justified.

Wetting tests have then been carried out thanks to a specific device, representative of a reflow process and led to a comparison between wetting behaviours under air and nitrogen. In parallel, reliability of boards have been evaluated thanks to contaminants tests: a BONO corrosion test, and a SIR test, modified to be more representative of today's boards designs.

Lead-Free Solder Pastes Wetting Tests

New solder pastes formulations have been developed by pastes manufacturers in order to limit oxidation phenomena and to obtain the same behaviour under air and under nitrogen. Evaluation of wetting performances of several lead-free pastes and analyse of the behaviour differences have been achieved in this article. Besides traditional lab-scale methods to evaluate soldering performances – spreading test and wetting balance test -, a new commercially available equipment has been designed to reproduce as far as possible the real reflow processes conditions. This equipment, SP2 from Malcom Instruments, is the one we used for this study. Improvements works have been realized by Air Liquide and IFTEC to get an accurate simulation of reflow ovens temperature cycles.

Experimental Set-Up and Methodology

This new test device is shown on Figure 1 with a schematic view of the tester principle on Figure 2.

It appears from the sketch that the upper part of the device is quite close from those of a standard wetting balance. On the lower part, the surface of the solder bath is replaced by a board on which a small amount of paste is printed. The solder bath itself is replaced by a heating element, on which the board is fixed. This heating plate allows the set-up of reflow oven temperature cycles. The whole zone test is equipped with a dry box enclosure and inert and hot gas supply. With this apparatus, a residual oxygen level of 50 ppm can easily be reached. When the test begins, the copper sample (grade IV according to ISO9455-16 standard) is placed at the surface of the paste. The temperature profile starts and the forces occurring on the sample are measured.

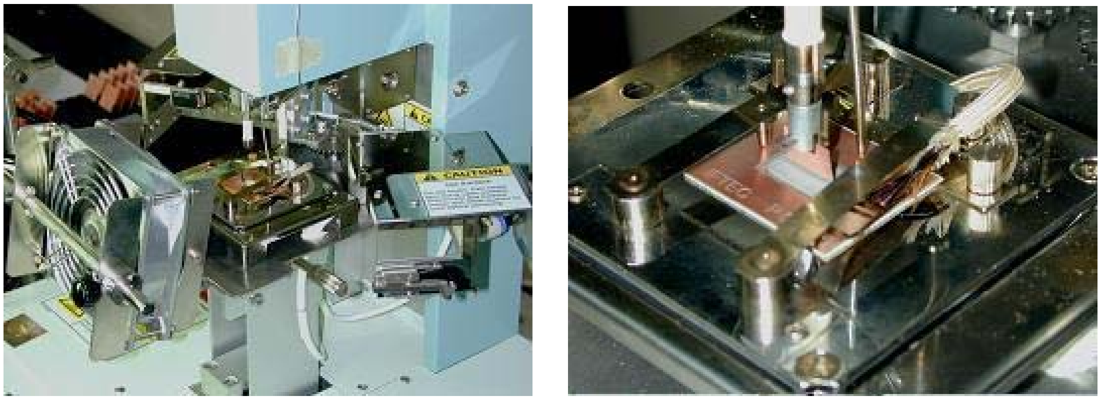

Figure 1 - Solder Paste Tester SP2 from Malcom Instruments – View of the Test Zone on the Left – View of the Sample on the Right

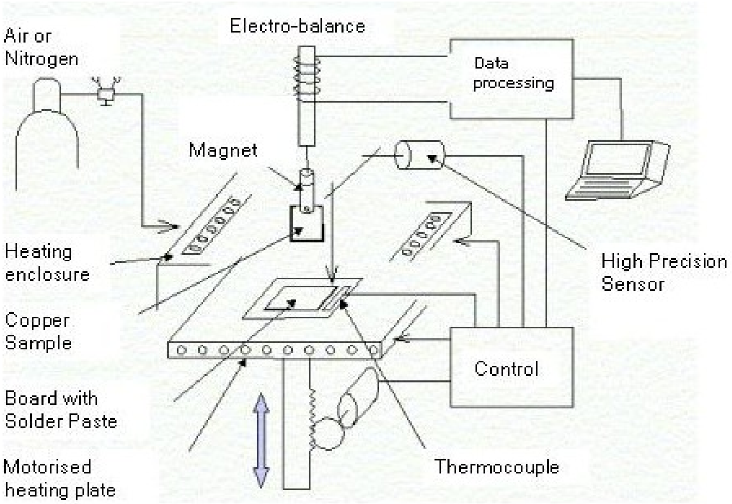

Figure 2 - SP2 Device – Operating Principle

All the modifications made to adapt this equipment to reflow temperature profiles, as well as the whole procedure, have been already described in previous publications.[2]

Tests Results and Discussion

The tests were performed with 7 lead-free "no clean" solder pastes that were chosen according to their emergence as the best candidates for reflow applications, the alloys contents of the 7 pastes being close to Sn96,5Ag3Cu0,5. Those pastes have also been selected in order to get a wide range of wetting behaviours and a representative sample of solder suppliers, named A,B,C, etc. In the whole study, pastes are represented by letters A, B, C, pastes B+ and C+ said by the supplier as being more activated than respectively pastes B and C. The soldering profiles chosen were recommended by solder suppliers. The main characteristics of these pastes can be seen in Figure 3.

Wetting forces and time have been measured under air and under nitrogen, and for each case, 10 measurements have been realized. According to ISO 5725-2 relative to the application of Grubb Criteria, only values comprised in a 5 to 95 % confidence interval have been selected among the 10 measurements.

Wetting force results are collected on Figure 4. The results under air and nitrogen are compared for each paste. Confidence intervals have also been reported to evaluate the results homogeneity in each case.

	Alloy Composition	Metal Content %	Flux Classification (J-STD-004)	Melting Point °C
A	Sn95,5 Ag4 Cu0,5	88	L0	217
B	Sn95,5 Ag4 Cu0,5	88	REL0	217
B +	Sn95,5 Ag4 Cu0,5	88	REL1	217
C	Sn96 Ag3,75 Cu0,25	89,1	REL1	217
C+	Sn96 Ag3,75 Cu0,25	89,1	REL1	217
D	Sn96,5 Ag3 Cu0,5	89	ROL0	217-220
E	Sn96,5 Ag3 Cu0,5	88,5	ROL0	217

Figure 3 - Lead-Free Solder Pastes Characteristics

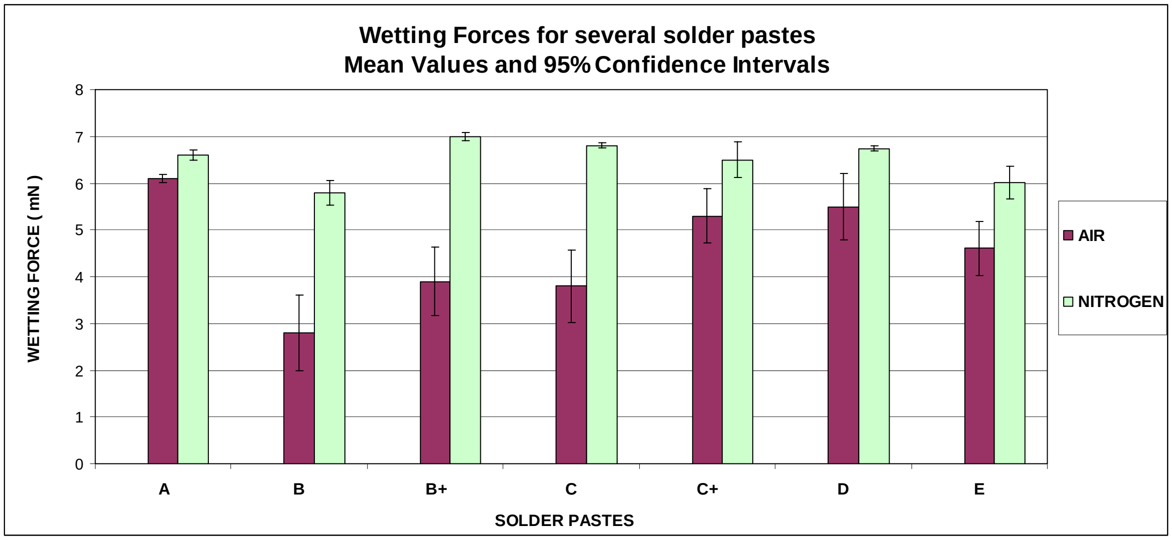

Figure 4 - Wetting Forces Measurements on SP2

First of all, we can see from confidence intervals that nitrogen improves the wetting process stability, precision and repeatability of the results.

In addition, wetting forces, in all the cases, are greater (or nearly equal) under nitrogen than under air : every paste remains in the same range of wetting force (5,8 - 7 mN), whereas the same pastes have a different behaviour under air where differences are emphasized (2.8 – 6 mN).

The point that has to be underlined, is the behaviour differences between solder pastes in regard to wetting atmosphere. It thus appears from Figure 3 that whereas nitrogen is of greatest interest for pastes B, B+ and C, its effects are minimized for pastes C+, D and E and are even negligible for paste A which exhibits very high wetting forces under air.

These gaps between solder pastes are probably linked to differences in pastes formulations, and more particularly on activators quantity or composition.

To bring quantitative data to support this analysis and to clarify these preliminary results, contamination tests have been realized.

Contamination Tests

Highly activated formulations may lead to the formation of post-soldering residues: flux components may oxidise or polymerise, electomigration phenomena may occur, thus making these residues harmful if left on the end-product.

As a consequence, several tests are used in the industry to characterize not only the residue amount but also their effects on final products reliability. However many works showed that current methods can frequently falsely predict the effects of residues remaining on the board and are not always representative of today's assemblies processes.[3]

That is the reason why this study presents a comparison of two residue tests results. The two tests identified are the well-known SIR test, widely used in the electronic industry, and a corrosion test, the BONO test, known to be more severe and more selective to predict assemblies reliability.

Corrosion Test: BONO Test Principle

The BONO test has been developed to assess of soldering flux corrosivity and has been adapted for solder pastes evaluation.[4] This test uses a printed circuit board carrying a copper track test pattern which consists of 10 electrolytic cells each having a very narrow anodic track running between two broad cathodic tracks. Anodic and cathodic tracks have well defined dimensions and the nominal resistance of the anodic track is about 6Ω. The tenth electrolytic cell has no central track and is used as reference. Only the cathodic track is coated with solder paste and solder mask is used on the anodic track. After reflow soldering, the boards are placed in a chamber under a 85°C/85%HR atmosphere during 15 days and the electrolytic cell is polarised under 20V. A test piece is shown on Figure 5 after soldering.

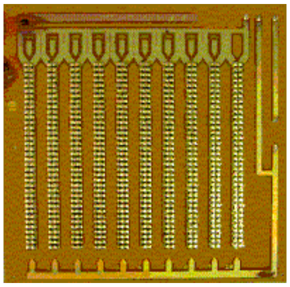

Figure 5 - BONO Test Vehicle

The anodic track resistance is measured before and after the test, and the corrosion factor is defined as the relative variation of this resistance and will be an indicator of corrosion and electromigration phenomena occurring on the board.

BONO Test Results

The 7 solder pastes characterized in terms of wetting performances have been tested: pastes A, B, B+, C, C+, D and E, and have been soldered under air. At the end of the test, the resistances of each anodic track are measured and a correction factor is applied to take into account the uncertainty on tracks dimensions. With this correction, the corrosion factor is calculated as if the initial resistance was equal to the theoretical initial resistance of 6 ▯In the same way than for wetting forces, ISO 5725-2 has been used to select only the results comprised in a 5 to 95 % confidence interval, and for each test condition, the mean value and confidence interval of the set of nine measures have been calculated.

The results are presented on Figure 6.

Prior to analysing the results, it should be noted that the BONO test procedure do not specify any real critical value above which we can consider that we fail the test. This critical limit depends on industrials internal specifications. If high quality products are targeted, this limit can be placed as low as 5%, otherwise the critical corrosion factor is usually placed at 8%

As shown by Figure 6, the first result that has to be pointed out is the one from solder paste A: no corrosion factor measure is associated to this paste since the tracks broke before the end of the test, thus revealing a very high corrosion level and the presence of harmful flux residues.

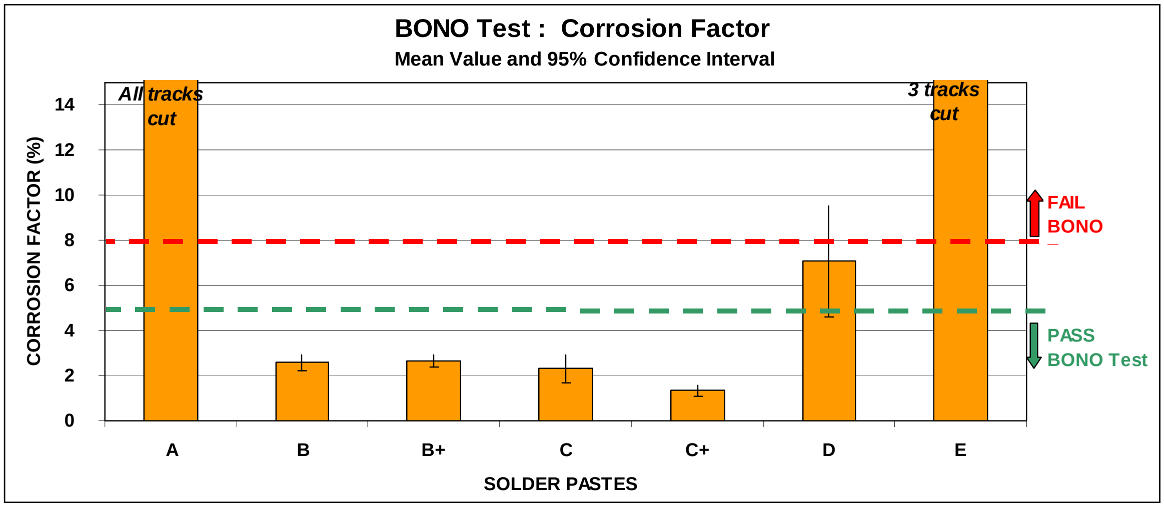

Figure 6 - Comparison of BONO Test Results for the 7 Solder Pastes under Test

If we consider the four other pastes, we see that pastes B, B+,C and C+ show corrosion factors around 3% and by then are all under the generally established critical corrosion factor. Paste D shows a high uncertainty and a corrosion level higher than those observed for B and C pastes families. Paste E, with 3 tracks cut, fails the test and reveals the effects of harmful residues left on the board.

Moreover, although the objective of the BONO test is not to compare the impact of air and nitrogen on contaminants level, the tests have also been performed after nitrogen reflow soldering. It appears from the results obtained that corrosion factors are in some cases slightly higher for nitrogen, without modifying pass/fail results of the pastes. Further study would help to confirm the explanation that under nitrogen, better wetting and spreading performances of pastes are obtained, thus allowing a larger surface of the anodic track to be in contact with residues.

All wetting and BONO results have been gathered on Figure 7, so wetting performances under air and corrosion levels can easily be compared.

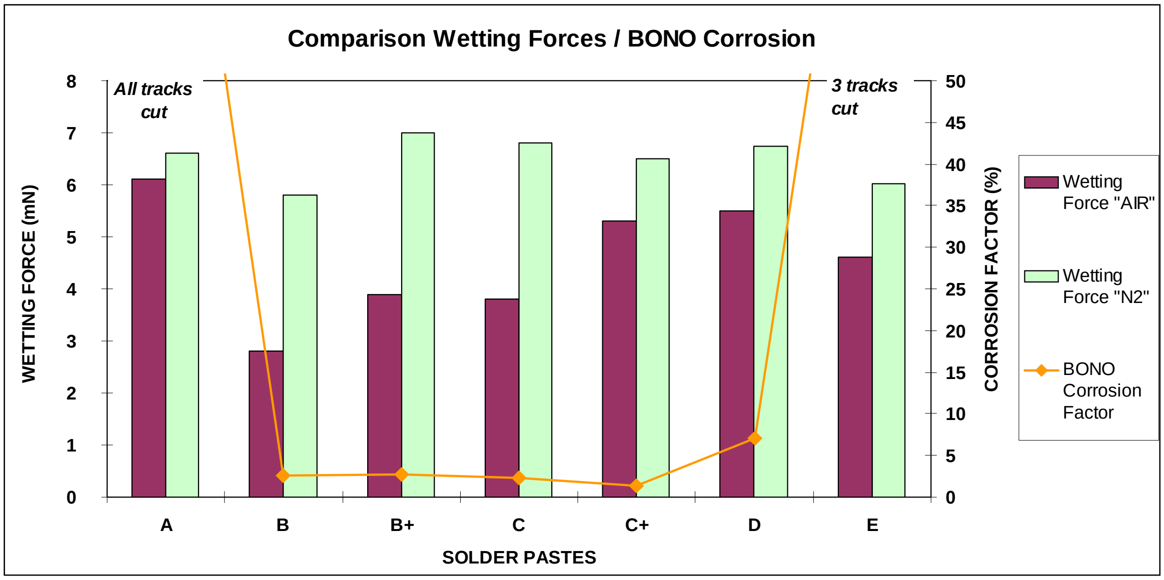

Figure 7 - Comparison between Wetting and BONO Results

This graph clearly shows that Paste A, with very good wetting performances under air, is much more submitted to corrosion effects than pastes with lower wetting performances under air. Thus, we see that the lowest the wetting difference between air and nitrogen is, the highest the corrosion level is: pastes D and E wetting forces under air tend to be as good as under nitrogen, but BONO results are much higher than for pastes families B and C.

Figure 8 helps to illustrate this effect by showing the appearance of two boards after the test, the board soldered with paste A under Air and the board soldered with paste B under nitrogen. Paste A board reveals the presence of flux residue traces spread on the board -clear yellow glints - , as well as high level corrosion zones in dark green on the copper tracks. On the opposite, paste B under nitrogen shows a much cleaner appearance, for a same level of wetting performances.

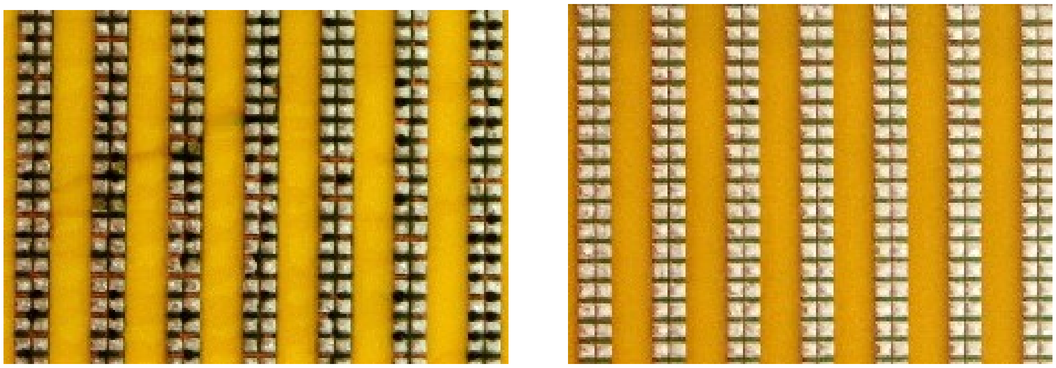

Figure 8 - BONO Test Vehicles – Air Soldered with Paste A to the Left and Nitrogen Soldered with Paste B to the Right

Surface Insulation Resistance Test
The second test performed is the well-known SIR test. It consists in measuring the degradation of the electrical resistance between two interdigitated combs, after printing with solder pastes while submitted to a hot and humid environment. An example of a test board is shown in Figure 9.

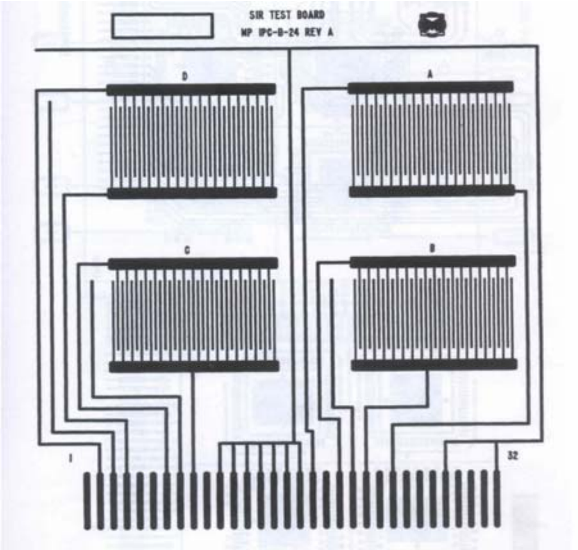

Figure 9 - IPC TM-650 SIR Test Vehicle

Although this test has been used in the electronic assembly industry for many years for incoming inspection and for prediction of long-term failure mechanisms, it now seems inappropriate from various points of view. Indeed boards, designs and industry processes have drastically evolved and SIR test board, such as IPC-B24, is no more representative of today's electronic assembly industry. For example, the spacing between comb fingers, as well as the width of each comb of a SIR B24 pattern, is far from the current fine pitch. Moreover, the IPC-B24 Standard test board is described by IPC Handbook version of 1996 as "seldom representative of actual products" and as offering "no challenge for reflow profiles".[5] However, this test pattern is still the most commonly used to predict pass/fail criteria.

Recent research works are carried out to adapt the test parameters, such as the test pattern spacing, the temperature and humidity conditions, the test voltage, the frequency of measurements.[3]

In the present study, our objective was to perform a severe enough SIR test to be able to differentiate pastes behaviors and to have a good indicator of the residual contamination remaining on the boards. Slight modifications have then been made based on the IPC-B24 test board design. The gap between the comb fingers is the factor expected to have a main influence on the SIR response, as a consequence it has been reduced from 500 microns to 200 microns. Following IPC-TM-650 2.6.3.3, the test boards were placed 168 hours in a 85°C/ 85%RH environment. The test voltage was 100V and the polarization voltage – 25V (lowered to be adapted to the gap reduction, following IPC Standard 22-21). Measurements have been done at 0, 24, 96 and 168 h. The main test conditions are summarized in Figure 10 and compared to IPC SIR Standard.

	IPC-TM-650 2.6.3.3	Air Liquide SIR
Test Voltage	100 V	100 V
Bias Voltage	50 V	25 V
Polarity	Reverse	Reverse
Environment	85°C / 85%RH	85°C / 85%RH
Duration	7 days	7 days
Board surface Finish	Bare Copper	NiAu
Lines / Spacing	0,4 / 0,5 mm	0,4 / 0,2 mm
Number of squares	~ 1000	~ 1000

Figure 10 - SIR Test Parameters

SIR Test: Results

Only 5 solder pastes among the 7 tested with the BONO test could be characterized with the SIR test. 3 boards with 4 comb pattern on each board have been used to characterize each test condition after air reflow soldering. In the same way than for wetting forces and BONO test, only results comprised in a 5 to 95 % confidence interval have been selected, and for each test condition, the mean value and confidence interval of the twelve measures have been calculated.

Only the measures at the end of the test, after 168 hours, are presented in this document in Figure 11.

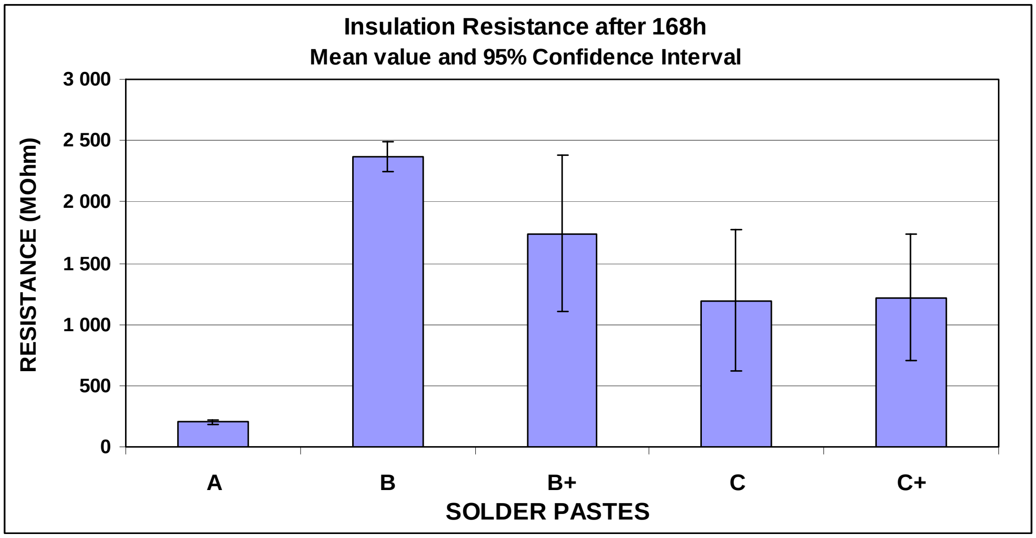

Figure 11 - SIR Test Results after 168 Hours

First of all, the results obtained reveal a quite important dispersion, especially for pastes B+, C and C+ which exhibit uncertainty around 50%, whereas pastes A and B results are given with an uncertainty below 10%.

What should be noticed is the poor level of paste A resistance after the test, when compared to paste B, which has the best resistance value. Considering the high uncertainty on pastes B+, C and C+, no real trend can be expected.

In the same way than for BONO test, measurements have also been performed after nitrogen reflow soldering. Resistance measurements are each time slightly better with nitrogen; further study would help to understand the effects of atmosphere on SIR results.

Discussion on Wetting and Contamination Results

To help for the results analysis, wetting, corrosion and SIR results have been gathered. On Figure 12, wetting results under air and nitrogen are compared to corrosion and SIR results under air.

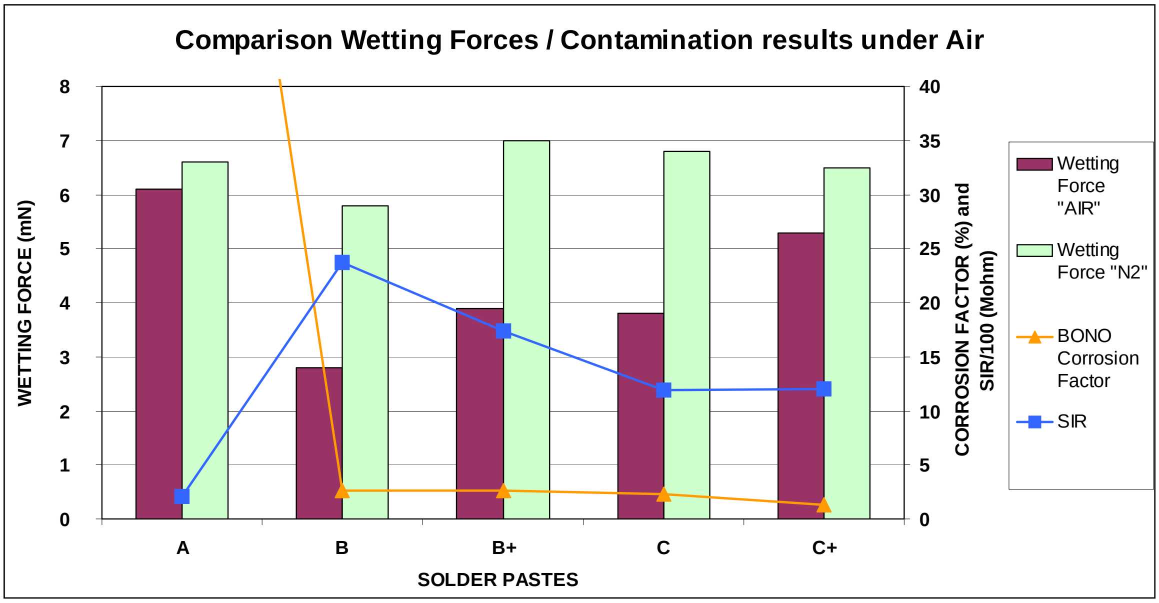

Figure 12 - Comparison between Wetting and Contamination Results under Air

This graph makes possible a correlation between, on the one hand, wetting forces differences under air and nitrogen, and on the second hand, an evaluation of residual contamination remaining on the board thanks to BONO and SIR test results.
First of all, we can notice that both corrosion and surface insulation resistance tests show the same trends: the lower the surface insulation resistance, the higher the corrosion factor. This tends to prove the validity of the method presented here to assess of contaminants effects, even if the results uncertainty is not always optimised.

Moreover, the interesting point is the comparison that can be made with wetting results : it thus clearly appears that pastes with good wetting results under air and consequently revealing a slight impact of nitrogen, are the pastes for which the contaminants effects are the most important : paste A is a good example of this phenomenon. On the opposite, paste B, for which the poor wetting performance under air is doubled with the use of nitrogen, shows the lower level or effect of contaminants. Paste B+, with more activators than paste B; see its surface insulation resistance decreased.

This study clearly shows that while the use of activators increases wetting performances, it also strongly impacts boards reliability on a long term basis. On the opposite, nitrogen offers the same level of wetting performances to low activated pastes, without the effects of activators residues.

Conclusion

First of all, the results presented here confirm the hypothesis that better wetting of highly activated pastes under air, leads to higher residue deposition levels. Thus, on a representative sample of 5 solder pastes, a correlation has been done between wetting performances under air and electromigration phenomena due to contaminants remaining on the board. As a consequence, even if some specific behaviours can not be fully explained and require further investigations, the main trend is that highly activated pastes use leads to the deposition of harmful residues.

The effect of these residues on assemblies reliability is also clearly shown thanks to contaminants tests. Moreover, the study reveals that wetting process is clearly improved and better controlled with an inert atmosphere.

Nitrogen use overcomes the lower wetting performances of non-activated pastes while keeping a low residue amount.

When end-product quality is targeted, nitrogen clearly appears as an attractive and environmentally-friendly alternative to highly activated solder pastes.

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