AIR PRODUCTS

Oxygen Concentration in the Soldering Atmosphere— How Low Must We Go?

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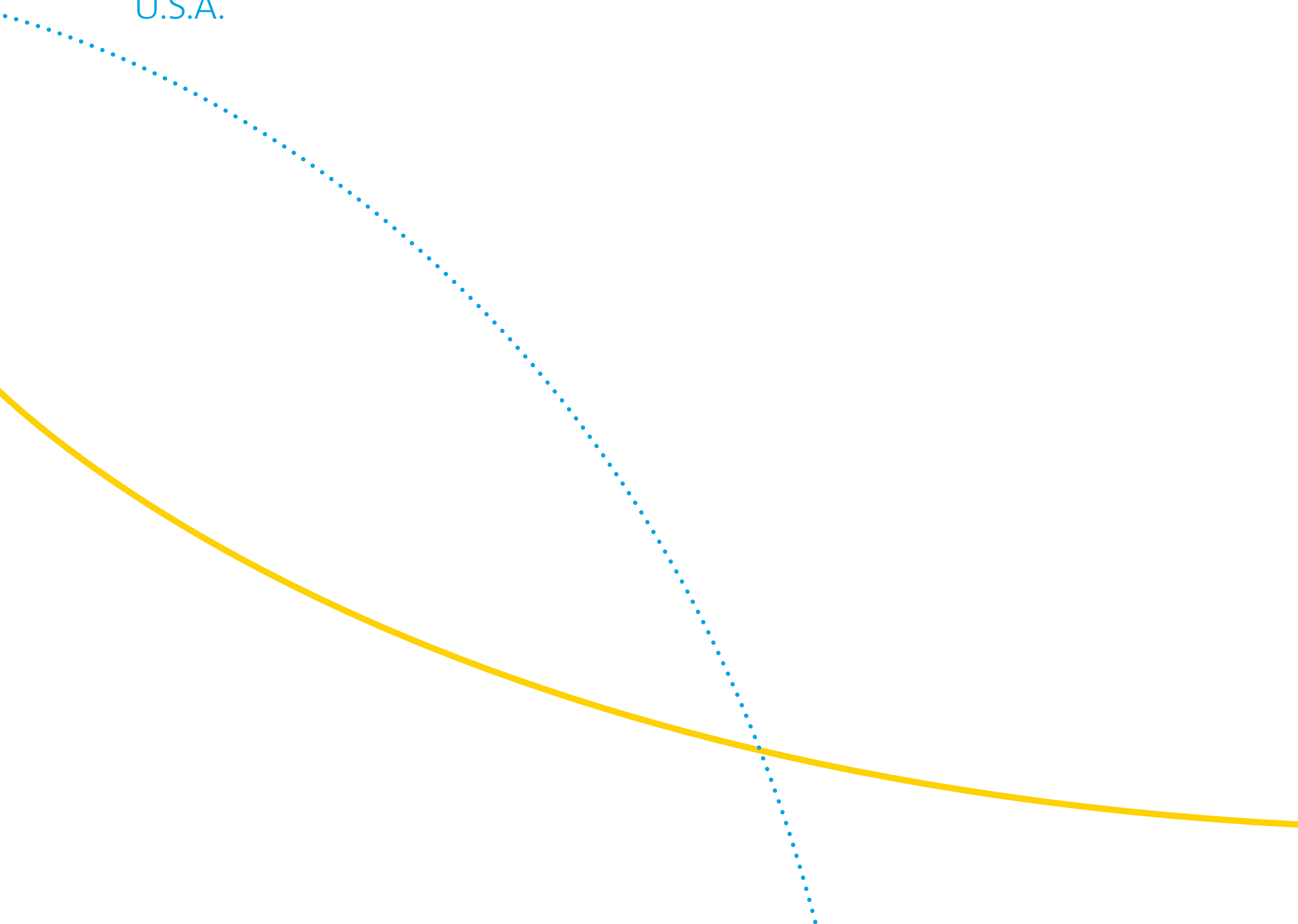


Abstract

An experimental study was conducted to understand the dependence of soldering defects on the inerting level and other reflow variables such as flux activity and solder particle size. The soldering defects investigated here are solder balls, nonwetting, solder joint bridging, component misalignment, and residues. The results verify that controlled-atmosphere soldering is very important in improving soldering quality. Soldering defects can be minimized by correctly adjusting the oxygen concentration in bulk nitrogen. Based on the results obtained in this study, a guideline in selecting the purity level of nitrogen was summarized. The experimental methods used in this study proved to be very effective in demonstrating soldering performance.

Introduction

In the past several years, the soldering technology of the electronic assembly industry has been undergoing revolutionary changes. These changes make controlled-atmosphere soldering more critical. One of the changes is based on the materials used for soldering to ensure environmental safety. This change includes not only the solder alloy but also the flux system. No-clean fluxes have become more attractive due to the elimination of chlorofluorocarbons (CFCs) as cleaning agents. Compared with conventional fluxes, no-clean fluxes are produced by using a smaller amount of activators to reduce residues. However, this approach also reduces flux activity; thus the oxidation on both solder and base metal becomes more of a concern since the oxides may reduce solderability.

Another change involves the package used for assembly to pursue a reduced size and cost. One of the industrial trends is toward the use of finer pitch Surface Mount (SM) devices. For this fine-pitch (< 25 mil) technology, solder pastes with a smaller particle size (< 80 μm) are required to ensure printing quality. However, this reduction in particle size increases the oxidation tendency of the solder due to an increased surface-to-volume ratio on each particle, thus affecting soldering performance. On the other hand, the conducting traces made of bare copper are preferred for fine-pitch soldering because the copper reduces coplanarity problems as compared with a tinned surface. However, a bare copper surface is readily oxidized and solderability is always an issue. Therefore, to reduce these oxidation problems, especially encountered in the no-clean and fine-pitch technologies, nitrogen-based inert atmosphere soldering has received more and more attention.

In conducting nitrogen soldering, however, questions still exist, such as: "What is the optimum oxygen level?" The optimum oxygen level corresponding to the best soldering performance and the lowest cost is actually a function of various soldering variables. Even under a specific soldering condition, the optimum oxygen level still varies with the type of soldering defect to be considered. Therefore, in this study, an experimental matrix for reflow soldering was designed to understand the dependence of each soldering defect on the inerting level and other reflow variables such as flux activity and solder particle size. The soldering defects investigated here are solder balls, nonwetting, solder joint bridging, component misalignment, and residues.

The experimental results provide convincing evidence on the benefits of controlled-atmosphere soldering and a guideline in selecting the purity level of nitrogen.

Reflow Variables

Reflow Environments

This study includes both a laboratory investigation and a production-scale evaluation. In the laboratory investigation, a thermogravimetric analysis (TGA) system, an optical microscope with a thermal stage, and a quartz tube furnace were used. Besides the capability of establishing a required temperature profile, each system has a sealed chamber where a desired oxygen concentration in bulk nitrogen can be maintained. In the production-scale evaluation, an RTC IR reflow furnace with an installed gas flow panel was used. In this furnace, nitrogen atmosphere containing various amounts of oxygen could be introduced throughout each zone of the furnace. The furnace has four heating zones, which allow us to obtain the reflow profiles recommended by solder paste manufacturers.

Solder Pastes

The flux activity in a solder paste depends on the type of activator used. With the same activator, the flux activity decreases with decreasing solid content, or nonvolatile matter (NVM), in the flux. In this study, two types of halide-containing solder pastes with different NVM levels were used, i.e., rosin mildly activated (RMA) and low-residue (LR). In addition, a halide-free solder paste, which is water-soluble (WS), was also used. To evaluate the effect of solder particle size, three RMA solder pastes with different particle sizes were tested. Totally, five solder pastes (all from Alpha Metals Inc.) were used in this study, as summarized in Table 1.

Circuit Boards

Since the copper traces on a circuit board are easily oxidized, copper protective coatings are widely used in the soldering industry. To correlate our research with the industry, the circuit boards used in our study were also coated (by Enthone-OMI Inc.) for preserving solderability. The coating was applied by the conveyorized flood immersion technique, which produces a uniform coating surface. To implement our research plan, the circuit boards (made by R&D Circuits) used in the production-scale evaluation were designed to have two different pitches and relatively long pads (Figure 1).

Table 1: Five solder pastes investigated

Solder pastes (NVM%)	Average particle size (µm)		
RMA (7%)	25	50	80
LR (5.5%)		50	
WS (halide-free)		50	

Figure 1: Schematic drawings of the two conducting patterns, (a) and (b), used in the production-scale evaluation.

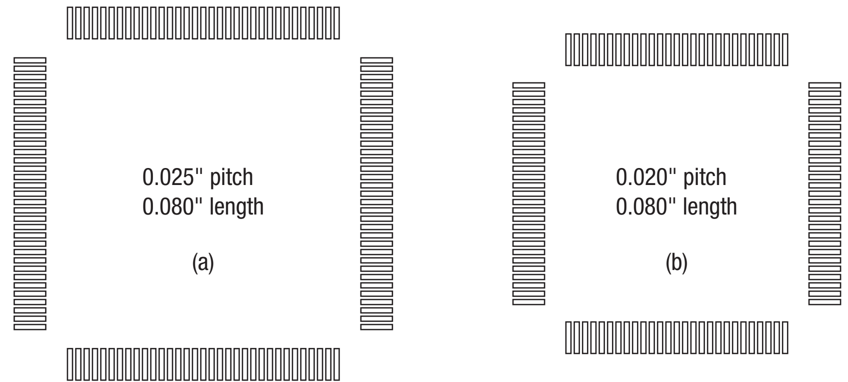
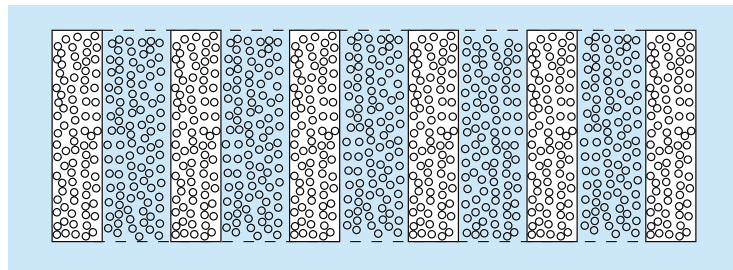


Figure 2: Schematic drawings showing "cross printing" of solder paste on trace area of a circuit board.



Defect Investigations

Solder Balls

Noncoalescent solder balls, which usually surround the solder pads, are caused by insufficient fluxing. This problem is aggravated by using ultra-fine powder in the paste, such as for the fine-pitch application, and is more of a concern when the no-clean approach is applied since the chance to remove the balls by post-reflow cleaning does not exist.

To accurately estimate the density of the solder balls as a function of oxygen concentration and solder particle size, samples were prepared by "cross printing" solder paste on the trace area of a circuit board (Figure 2), which was then heated up in the tube furnace. After solder melting, the molten solder automatically withdraws to the conducting pads, thus leaving noncoalescent solder balls on the solder mask area. The solder balls on each sample were photographed using an optical microscope.

As shown in Figure 3, for the RMA solder paste with a particle size about 25 µm, the density of the solder balls increases slightly with increasing the oxygen concentration when the oxygen concentration in the furnace is below 10,000 ppm. However, as the oxygen concentration is increased above 10,000 ppm, the density of the solder balls increases significantly. When this solder paste is reflowed in air (210,000 ppm), the density of the solder balls is extremely high, such as 400/mm2. For other solder pastes investigated, however, the particle sizes were much greater than 25 µm (50 or 80 µm), and the density of the solder balls was found to be relatively low (< 40/mm2) and insensitive to the atmosphere condition. The result obtained here is quite reasonable. As the particle size in a solder paste decreases, the surface-to-volume ratio of each particle increases, which promotes solder oxidation, thus decreasing the coalescent force and increasing the density of the solder balls.

Solder Spread

The extent of solder spread is an important parameter to estimate nonwetting tendency. In the laboratory study, the extent of solder spread on copper was investigated inside the tube furnace. This investigation was done by measuring the spread distance of a solder on a single copper line (2 mm wide trace on an epoxy board) rather than estimating the

Figure 3: Density of the noncoalescent solder balls formed on the solder mask area as a function of oxygen concentration in the reflow environment.

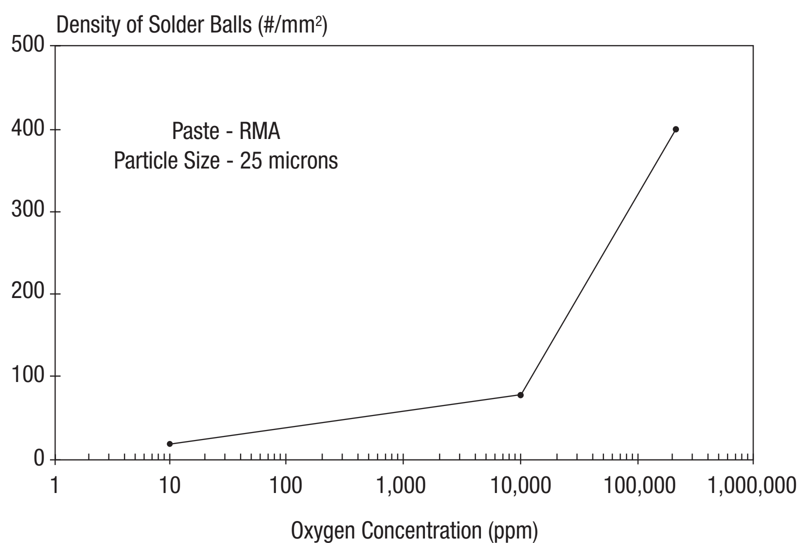
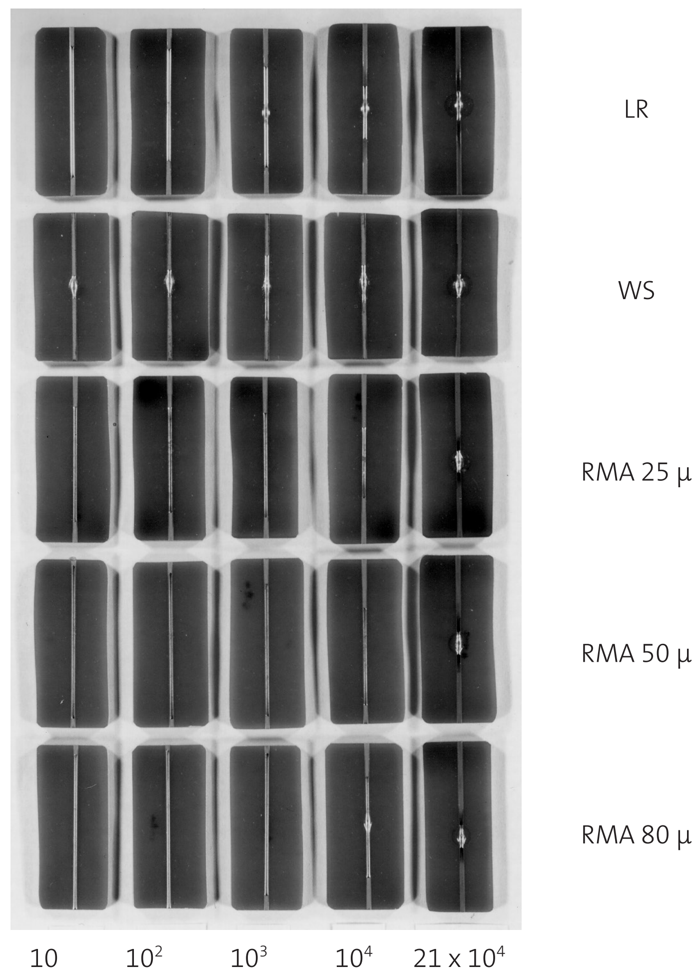


Figure 4: Optical photographs showing the spread of solder pastes on the copper trace under five reflow atmospheres.



spread area of the solder on a plain copper surface (an old method). This improved method greatly enhances the sensitivity of solder wetting to the changes in the soldering environment and improves the accuracy of the experimental results. This can be explained as follows. When a solder paste spreads on a uniform copper surface, both solder and flux spread together along all directions. The flux forms an envelope, which prevents solder oxidation, and the flux at the spreading front removes oxides from the copper surface, thus making solder spread relatively insensitive to the reflow environment. However, when a solder paste spreads on an epoxy board with a single copper trace, the spreading of the molten solder is restricted along the narrow copper line, where the intermetallic formation drives solder wetting. At the same time, the flux in the solder paste spreads uniformly on both epoxy and copper surfaces, thus causing a separation between the flux and the solder and making the solder spread more sensitive to the oxygen concentration. This spread pattern is typically encountered in the solder reflow on a printed circuit board and was therefore used in this study.

Figure 4 shows the spread of each solder on the single copper trace under five reflow atmospheres. The spread distances of the solder pastes versus oxygen concentration are plotted in Figures 5 and 6. For most of the solder pastes investigated, the extent of solder spread decreases significantly when oxygen concentration is above 1000 ppm. This indicates that the oxidation of copper becomes severe when the oxygen concentration is above 1000 ppm. In contrast, for WS paste, the extent of solder spread is optimized at an oxygen concentration of about 1000 ppm. This spread behavior of having an optimum oxygen concentration was occasionally observed (Ref. 1). A possible explanation for this phenomenon can be described

Figure 5: Spread distance versus oxygen concentration for RMA, LR, and WS solder pastes with a particle size of 50 µm.

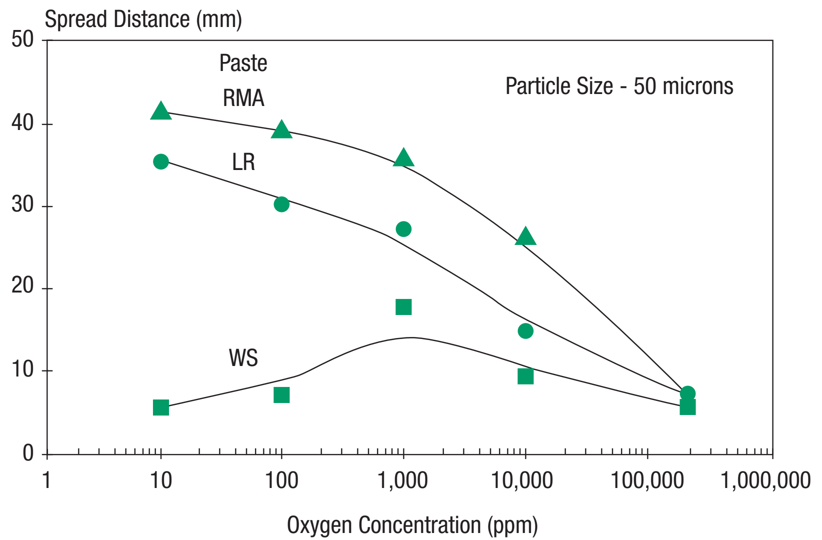
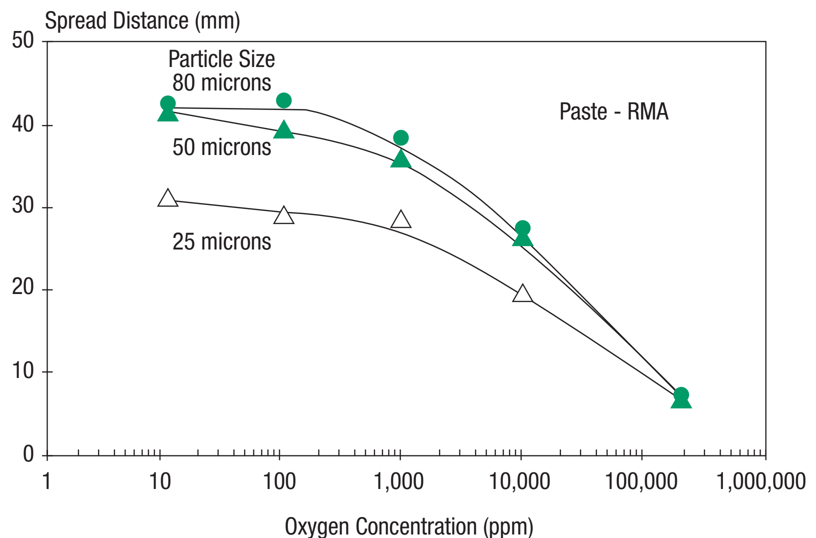


Figure 6: Spread distance versus oxygen concentration for RMA solder paste with various particle sizes..



as follows. The presence of oxygen in the molten solder (below the solubility limit) reduces the surface tension of the solder, which improves wetting. On the other hand, with increasing oxygen concentration, the copper surface becomes more oxidized, which inhibits wetting. Both of these effects dominate solder wetting for the WS paste (instead of only the second effect dominating wetting for the other solder pastes). Therefore, a combination of these two effects results in an optimum oxygen concentration.

In the production-scale evaluation, the spread of each solder paste on the printed circuit board was studied by using the IR reflow furnace. As shown in Figure 7, the solder paste was transferred to the copper trace by "fractional printing" with a stencil opening of 40%. After soldering, the percentage coverage of the solder on the pads was then estimated. As shown in Figure 8, the result is quite consistent with laboratory findings.

Debridging Tendency

With an acceptable printing quality and volume, the solder joint bridging is normally caused by slumping of the solder paste on adjacent pads before reflow. This defect is most often encountered in fine-pitch devices. During reflow, the molten solder will pull back on each pad if the extent of solder spread is relatively large and the resistance of the solder surface tension is relatively small. Both of these factors, the solder spread and the surface tension of the molten solder, vary with the soldering environment.

To demonstrate the effect of solder spread on debridging tendency, samples were prepared by "fractional joint printing" the solder paste on every adjacent two pads with a stencil opening of 40% (Figure 9). Each sample was reflowed in the tube furnace

Figure 7: Schematic drawings showing "fractional printing" of solder paste.

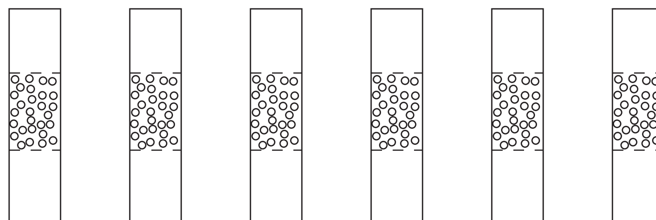


Figure 8: SPercentage coverage of solder on the pads versus oxygen concentration for RMA, LR, and WS solder pastes. Samples were reflowed in the IR furnace.

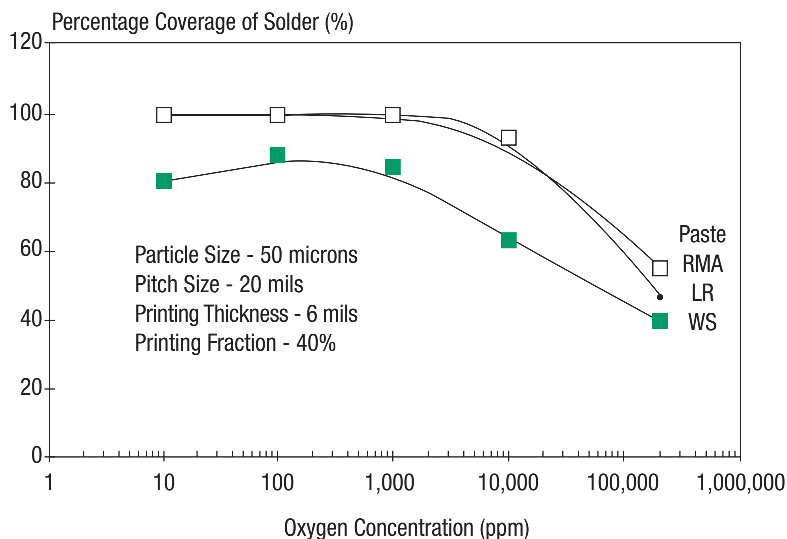
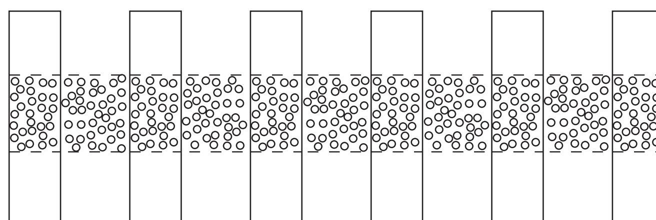


Figure 9: Schematic drawings showing "fractional joint printing" of solder paste.



with a desired inerting level, and then the percentage of debridging was counted. As shown in Figure 10, the percentage debridging for both LR and RMA pastes decreases with increasing oxygen concentration. However, for WS paste, there is an optimum oxygen concentration for maximum debridging tendency. Comparing Figure 10 with Figure 5, the debridging tendency and the extent of solder spread for each solder paste follow a similar trend with varying oxygen concentration. To further confirm this observation, the experiment was repeated by using the IR reflow furnace for a number of samples with different printing volume (40 to 60% stencil openings). The result shows that the debridging tendency as a function of oxygen concentration varies with the volume of each bridge initially created (Figure 11), but the maximum debridging tendency is indeed associated with the largest extent of solder spread. In a real soldering process, the room for a solder to spread on the conducting pads may be quite limited (for a full printing), but the spread of solder on the component leads can also make a contribution to debridging.

To understand the role of the surface tension of the liquid solder in debridging in the case of eliminating solder spread, another similar experiment was conducted by "joint printing" the solder paste on the entire area of every adjacent two pads (Figure 12). In this case, solder spread is eliminated during reflow, so that the effect of the surface tension on debridging can be assessed. The printing thickness was controlled to a critical limit, such that partial debridging could be obtained, and the percentage of debridging could be shown as a function of oxygen concentration. The results are presented in

Figure 13. For the three solder pastes investigated, the percentages of debridging are insensitive to the oxygen concentration, and therefore insensi-

Figure 10: Percentage of debridging as a result of solder spread versus oxygen concentration for RMA, LR, and WS solder pastes. Samples were reflowed in the IR furnace.

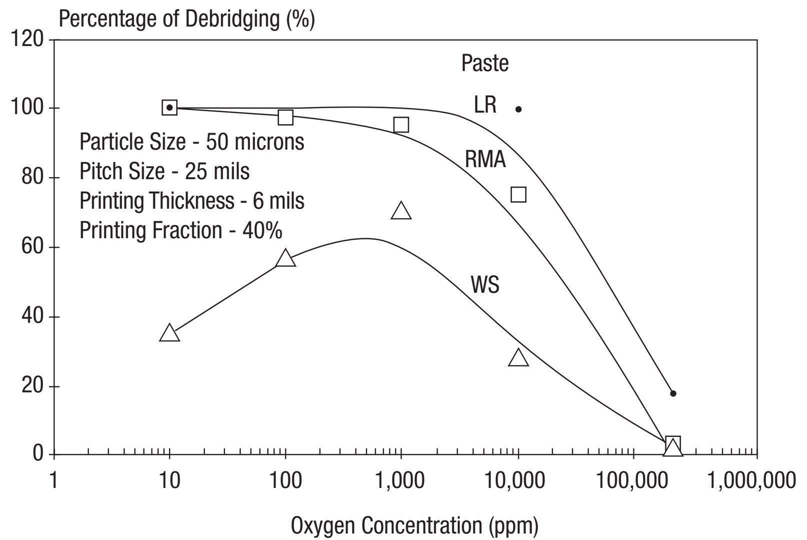
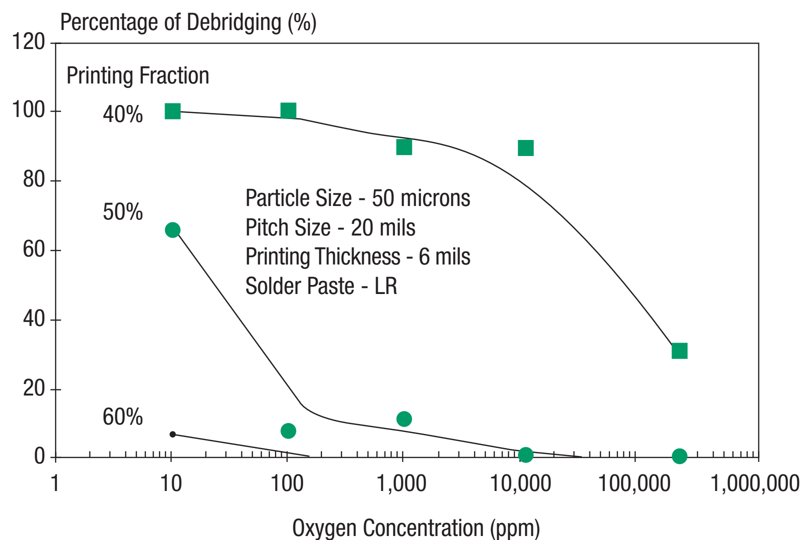


Figure 11: Percentage of debridging as a result of solder spread versus oxygen concentration for LR solder paste under various printing fractions. Samples were reflowed in the IR furnace.



tive to the surface tension change. It is understood that whether debridging occurs or not depends on if it reduces the surface area ($\Delta A < 0$) and hence the surface energy ($\Delta E < 0$) of the liquid solder. When the printing volume is below a certain limit, debridging normally occurs since it reduces the surface area of the liquid solder. Increasing the surface tension of the liquid solder ( ) increases the energy drop ($\Delta E = \Delta A \cdot$) from debridging, and therefore increases the driving force for debridging. However, in the case of excessive solder, debridging will increase the surface area of the liquid solder, which makes debridging energetically unfavorable. Figure 14 shows that at the critical printing volume, debridging decreases the surface area of the liquid solder only slightly. This observation indicates that varying the liquid surface tension cannot significantly alter the energy drop from debridging, and a small excess of solder will result in nondebridging. Therefore, when the solder spread is eliminated, debridging is more sensitive to the volume of the solder, and the surface tension of the liquid solder does not play an important role in debridging.

Figure 12: Schematic drawings showing "joint printing" of solder paste.

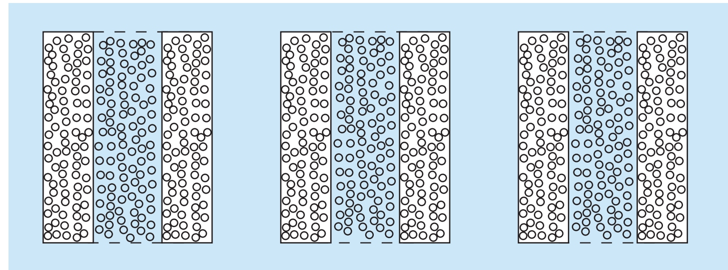


Figure 13: Percentage of debridging in the case of eliminating solder spread versus oxygen concentration for RMA, LR, and WS solder pastes.

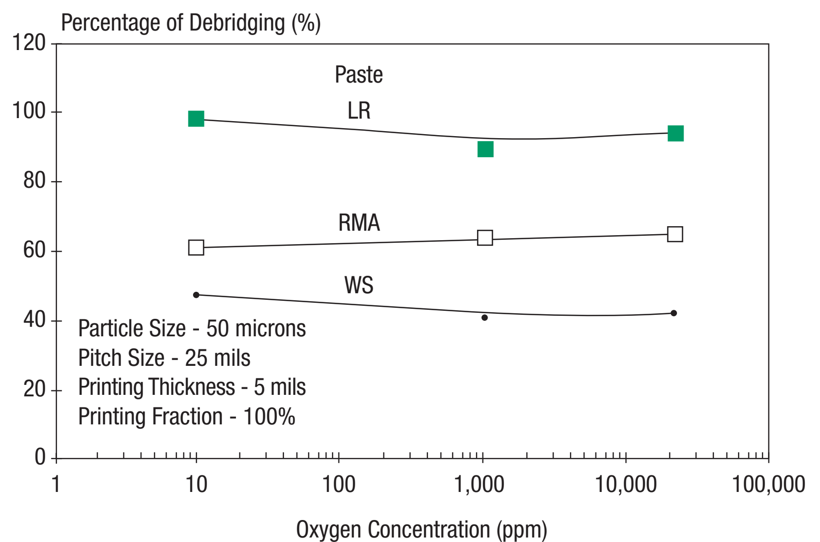
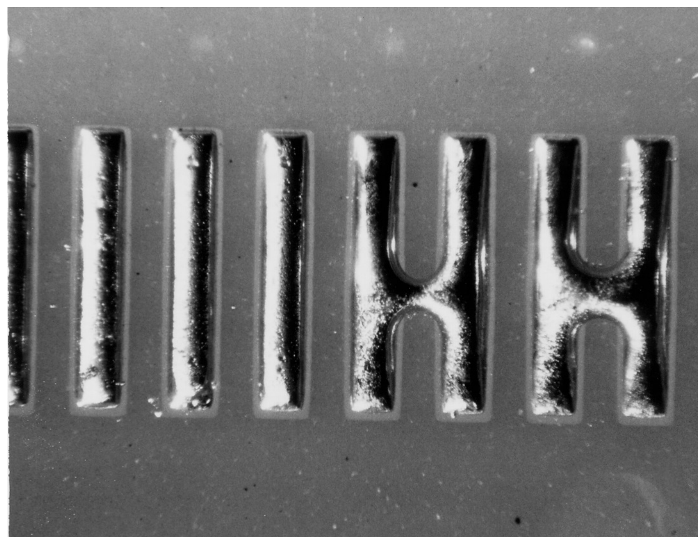


Figure 14: Optical micrograph showing partial debridging on a reflowed sample.

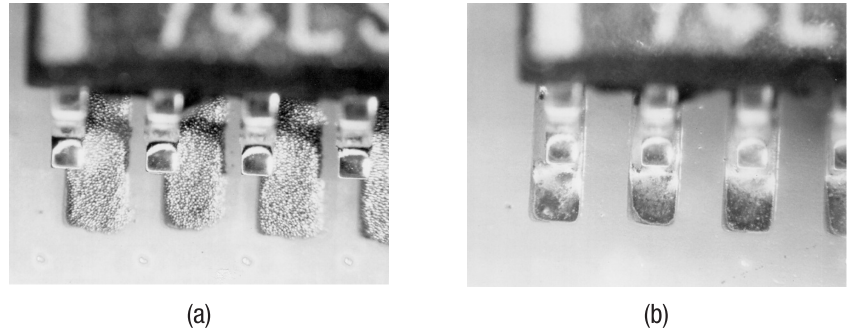


Component Realignment

Misalignment between the components and the printed traces on a circuit board is a common problem, especially when an automatic placing method is used. During reflow, the misalignment can be corrected if the surface tension of the molten solder is high enough. To study the realignment ability in response to the reflow environment, samples were prepared by placing a component on the trace area of a circuit board with a certain degree of misalignment which were then reflowed in the heating stage under various inerting levels. During each reflow, the realignment process was observed in situ under the optical microscope. The position of component leads relative to the pads was also photographed before and after each reflow, and the percentage of recovery was thus calculated.

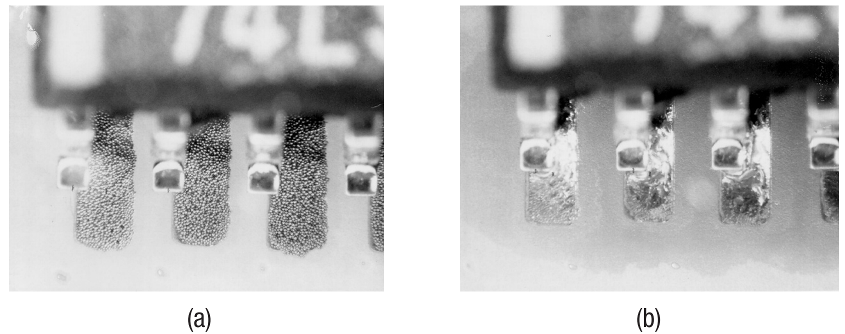
Figures 15 and 16 show a comparison of the component realignment in nitrogen (with 10 ppm oxygen) versus that in air. Although the initial degrees of the misalignment are about the same for both cases, 100% recovery is obtained in the nitrogen reflow, while only 50% recovery is achieved in the air reflow. The higher realignment ability in nitrogen is believed to be due to the higher surface tension of liquid solder, as a result of minimizing solder oxidation by nitrogen inerting. As presented in Figures 17 and 18, for all the solder pastes investigated, the percentage of recovery decreases with increasing oxygen concentration. For WS paste, this decrease in the percentage of recovery is very significant when the oxygen concentration is increased from 10 to 1000 ppm. This also confirms that the surface tension of WS paste is very sensitive to the surface oxidation.

Figure 15: Optical photographs showing component alignments (a) before reflow and (b) after reflow in nitrogen for WS solder paste.



(a) (b)

Figure 16: Optical photographs showing component alignments (a) before reflow and (b) after reflow in air for WS solder paste.



(a) (b)

Residue Level

With the increased use of the no-clean technique, the amount of flux residues left on the circuit board after reflow becomes more critical since post-reflow cleaning is eliminated. To investigate atmospheric effect on the residue level, a solder paste flux was melted inside the TGA system under an expected atmosphere, using a recommended heating profile.

Figure 19 shows the weight of the RMA solder paste flux as a function of time during a heating cycle to 220°C under three atmosphere conditions. Changing the inerting level from house nitrogen (10 ppm O_2) to normal air (210,000 ppm O_2) increases the weight of the flux residues about 10% of the initial flux weight. This observation can be explained as follows. Without oxidation, the flux can keep in the liquid phase and vaporize gradually with increasing temperature. The presence of oxygen, however, causes the liquid flux to either char or form solid residues, thus increasing the final weight of the flux. It also shows in Figure 19 that at an oxygen concentration around 10,000 ppm (one order less than air and three orders greater than our house nitrogen), the residue level is closer to that in nitrogen, which indicates that the increase in the residue level is accelerated when the oxygen concentration is increased to above 10,000 ppm. For LR solder paste flux, the residue level was found to be relatively insensitive to the oxygen concentration. The difference of the residue level between a nitrogen run and an air run is within 2% of the initial weight of the flux.

Conclusions

The experimental results presented in this paper provide an understanding of the dependence of soldering defects on the reflow variables, especially the inerting level. The results verify that controlled-atmosphere soldering is very important in improving soldering quality. Soldering defects can be minimized by correctly adjusting the oxygen concentration in bulk nitrogen. The acceptable (or optimum) oxygen concentrations to obtain a desired (or best) soldering performance for the five solder pastes investigated are listed in Table 2. These values may vary depending on a user's particular product and requirement, but can be used as a guideline. The experimental methods used in this study proved to be very effective in demonstrating soldering performance.

Figure 17: Percentage of recovery versus oxygen concentration for RMA, LR, and WS solder pastes with a particle size of 50 µm.

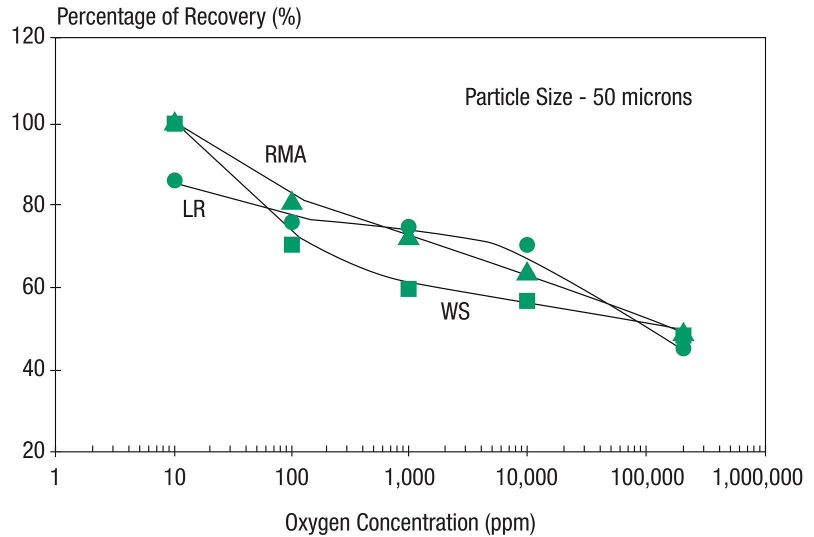
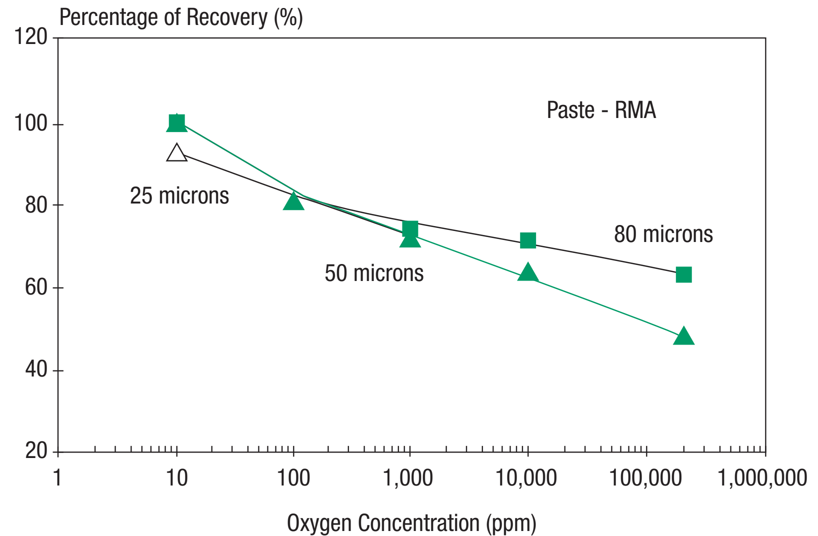


Figure 18: Percentage of recovery versus oxygen concentration for RMA solder paste with various particle sizes.



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Reference

C. C. Dong, A. S. Dawson, and M. S. K. Chen, "Effects of Trace Oxygen in Bulk Nitrogen on Solder Wettability," IPC Printed Circuits EXPO, P6-2 1–5 April 1994).

Figure 19: Thermogravimetric analysis showing the weight of the RMA solder paste flux as a function of time during a heating cycle to 22°C.

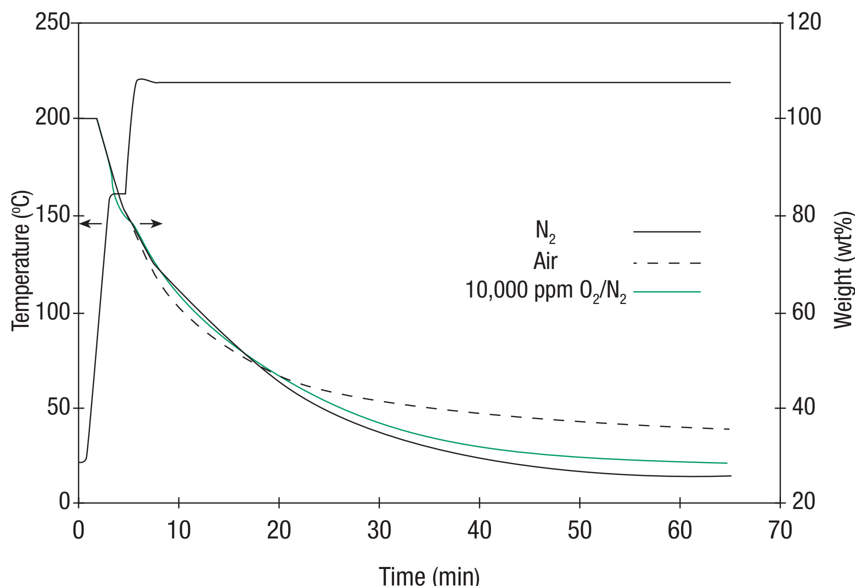

Table 2: Trial Parameters

Desired (best) soldering performance µm	RMA 25 µm	RMA 50 µm	RMA 80 µm	LR 50 µm	WS 50
low density of solder balls with less sensitivity to O_2 level	<1%	all	all	all	all
large (largest) extent of solder spread with less sensitivity to O_2 level	<1000 ppm	<1000 ppm	<1000 ppm	<1000 ppm	(1000 ppm)
high (highest) debridging tendency with less sensitivity to O_2 level	<1000 ppm	<1000 ppm	<1000 ppm	<1000 ppm	(1000 ppm)
>60% component realignment	<1%	<1%	<1%	<1%	<1000 ppm
small amount of residue with less sensitivity to O_2 level	<1%	<1%	<1%	all	
Overall	<1000 ppm	<1000 ppm	<1000 ppm	<1000 ppm	(1000 ppm)

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