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The
Magazine
for
Electronics
Assembly

June 2000
www.smtmag.com
PennWell

cover focus

PCB Outsourcing:

Technology & Business Focus

NITROGEN AND SOLDERING:
REVIEWING THE ISSUE OF INERTING

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INTRODUCTION

Using nitrogen to inert the atmosphere during soldering has by now become a generally accepted practice in electronic assembly. But whereas there seems to be little doubt in the minds of the user that nitrogen "improves" the wave soldering process, and that it actually 'pays its way' simply by reducing dross, its application in reflow equipment is still questioned frequently.

This insecurity, or sometimes even misinformation, about the use of nitrogen in reflow equipment persists despite a wealth of information and research on the hows and whys of nitrogen usage – applied to wave as well as to reflow soldering. To address this discrepancy, we found it opportune to re-examine the entire issue of inerting. Basing our judgment on published results, corroborated by secondary findings as well as research, a clear picture emerges as to when nitrogen may be used to advantage, why it will benefit the process and where limitations may be found.

NITROGEN: THE GAS

Nitrogen is a common gas found in the atmosphere. About 78% of the air we breathe consists of nitrogen. The rest is made up of oxygen, carbon monoxide, carbon dioxide, as well as traces of argon and other gases. The fact that animal life survives in air is an indication that nitrogen is non-toxic. But pure nitrogen does not sustain life, not because of any inherent toxicity, but rather because of a lack of oxygen. Hence, when using nitrogen, precautions must be taken to avoid a situation where nitrogen is present without the required amount of oxygen.

Nitrogen boils at about -320.4°F (-195.8°C) and hence liquid nitrogen as it may be delivered is very cold. Cold nitrogen also is heavier than air and thus may accumulate in low-lying areas, if it is given a chance.

The absence of oxygen in pure nitrogen and the fact that it does not readily react with common metals have earned it the designation "inert." It is this property that benefits the soldering process by protecting metal surfaces from oxidation during heat-up and assuring proper action of flux. Nitrogen is used in to displace oxygen because it is the cheapest gas on the market that is inert, or chemically unreactive.

Nitrogen is not manufactured in the proper sense but rather is extracted from air, giving us a zero-sum game as far as the environment is concerned. The nitrogen extracted from the air is returned to it, and the air is neither depleted nor enriched because of this circular process.

There are a number of different ways of extracting nitrogen from air. The most common is a freezing process, usually referred to as "cryogenic." A cooling process is used to liquefy the gas, which in a kind of reverse distillation process purifies itself because of the different boiling points of oxygen and nitrogen. More recent extraction techniques are on-site production and liquid-assist systems that use a special cryogenic process assisted by a small amount of liquid nitrogen. Other on-site generation systems include membrane process and pressure swing absorption.

With these different processes, it is possible to provide nitrogen from a purity of 95% to 99.99999% [0.1 parts per million (PPM)], depending on the need of the process. Obviously, the different processes and purities carry different price tags. The price is also affected by the amount consumed, the delivery system chosen, the distance from the manufacturing plant and many other factors. Since most assemblers require a high purity atmosphere (<1000 PPM), liquid nitrogen or liquid-assist on-site systems (Figure 1) are recommended for assembly operations[1].

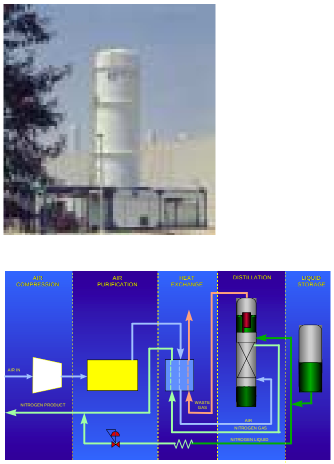

Figure 1: On-site N2 Liquid-Assist System

EFFECTS OF NITROGEN

In soldering, there are a number of basic phenomena caused by changing the ambient gas (air) to nitrogen. By examining these effects, including spreading behavior, wetting force, wetting angle and surface tension, we can see that nitrogen provides noticeable benefits that apply to both wave and reflow soldering.

Research examining the spreading behavior of solder under different environmental conditions has shown that spreading starts at lower temperatures as we reduce the ROL [Residual Oxygen Level]. In this study[2] we find that 63Sn/37Pb solder already spreads at 401ºF (205ºC) if the ROL is <10 PPM, but it needs 404.6ºF (207ºC) at 100 PPM and 518 ºF (270ºC) at 1000 PPM. The same pattern holds true for other solders and thus indicates an inhibiting property of oxides to the tendency of spreading.

Comparing wetting force for different fluxes in air and nitrogen again yields results indicating that nitrogen coverage can improve the process. Usually measured with a wetting balance, wetting force is an indicator of the quality and shape of the joint. A study[3] comparing a number of fluxes found that with a notable exception (adipic acid), the wetting force increases if measured under nitrogen rather than air. For some fluxes, the gain is substantial.

One measure applied to estimate wetting is the assessment of the wetting angle. Small wetting angles imply good wetting behavior and usually indicate a sound joint. When measuring wetting angles for a variety of fluxes, the same report found that for most, wetting angles were much smaller under nitrogen than in air. Thus nitrogen improves wetting for the large majority of flux vehicles employed.

The surface tension of the liquid solder plays a major role in the soldering process. It is responsible for the shape of the fillet as it counteracts the two other forces: wetting and gravity. As it is practically impossible to measure the surface tension of solder under air, we have to content ourselves with those measurements available to us, where a minute amount of tin oxide in the surface layer will falsify the measurement. Nevertheless, these measurements[3] again indicate that the surface tension is higher under nitrogen than under air. Since surface contaminants have a habit of reducing surface tension, however, the question is not entirely resolved. The tin oxide in the boundary layer may cause this difference in measurement. In practical application, however, experience shows that surface tension is lower under air than under nitrogen coverage.

An excellent demonstration of higher surface tension is verified by an experiment carried out in 1996 [4]. Looking at the amount of bridging left after reflow when solder pads were overprinted (40 percent coverage) using LR and RMA flux activation in the paste, the dependency on nitrogen coverage became apparent. Only under lower ROL values did the surface tension reach a high enough value to break the bridge and to collect all the solder on the pads only. An increase in wetting force may have aided, too.

The same article also investigated the relationship between oxygen deprivation and metal powder particle sizes in pastes. The current tendency towards fine pitch and the consequent use of paste with finer grain sizes increases the importance of such questions. Not only did the experiment confirm that nitrogen coverage improves solder spread in all cases, but it also showed that the finer the powder size, the more crucial it is to use an inert cover gas to achieve sufficient solder spread.

A somewhat puzzling result has been recorded[5] in a study related to wetting and surface tension. It may perhaps be understood best in the following way. If copper coupons are prepared that exhibit varying degrees of solderability and then tested under different environmental conditions (ROLs from 7 PPM to air), we find that those coupons that have excellent solderability perform about equally well under all conditions. However, those with lower solderability need less time to solder under low ROL conditions than under higher ones. That is, the spread of data (in statistical lingo, the variance or standard deviation) is greater under air than under better inerted conditions.

These test results are the explanation for the "increased process window" that everyone is talking about when addressing nitrogen soldering. The process becomes more forgiving under nitrogen than in air. Excellent solderability does not gain much from the absence of oxygen; it seems, however, even a minor deficiency in solderability benefits from inerting. In practical application, this means that if all the boards and components always have excellent solderability, then nitrogen does not significantly improve soldering parameters. In the more realistic case of varying solderability, however, the set of process parameters is much broader under nitrogen than it would be in air.

DRIVING FORCES BEHIND NITROGEN USAGE

Before we address direct implications for the two soldering processes, we should discuss broader industry trends that favor the use of nitrogen. One is the search for a superior surface finish on PCBs. Fine pitch demands better planarity conditions than HAL can offer. The use of Low Solids or No-Clean fluxes was the answer to the Montreal Protocol and the cleaning brain-teaser, but this does not make the search for a better surface any easier. The introduction of BGAs and the re-surfacing concern for joint quality also play into the surface issue. The complexity of the modern assembly is not only reflected in the number of layers of the board but also in the pressing need for multiple soldering processes or clever process modifications such as reflow soldering through-hole components.

It seems that OSP (Organic Solderability Protection – a collective name for some copper treatments such as Imidazole, etc.) used for a number of years with aggressive fluxes, can also provide an answer to these problems. Besides good planarity, it provides limited storage capability and certain price advantages. When LR fluxes are being used in multiple thermal excursion processes, however, OSP performs best when soldered under an inert atmosphere. There it may even outperform Ni/Au[6,7].

The question of the reliability of the soldered joint was underlined in a project supported by the German government[8] in which stress experiments yielded some unexpected results. Failure patterns in two components, A and B (different vendors), showed clear differences between those joints soldered in air versus those soldered in nitrogen. Whereas 183 failures of component A were recorded for joints soldered in air, only 3 were found for those soldered under nitrogen. The ratio of failures was also favorable for component B under nitrogen (air 302; 100 nitrogen).

Such findings are corroborated by other research, including a similar study performed at Siemens[10] and others in which the peel strength of joints was examined, again showing an advantage for those joints soldered under nitrogen.

WAVE SOLDERING UNDER NITROGEN

Now let us consider how nitrogen inerting affects the two processes, wave and reflow soldering. We will focus first on wave soldering, where nitrogen usage has become well established.

One of the primary differences between wave and reflow soldering is the creation of dross. Dross is formed in wave soldering when the molten wave of solder comes in contact with the oxygen contained in atmospheric air. Few users recognize that there are two distinctly different types of dross. On the one hand, there is the silvery sludge that covers the surface. It consists mainly of good solder and some tin oxide and may, with reservations, be deemed largely “harmless.” At turbulent spots and around the pump shaft, however, one may observe some black powder. This is the second type of dross that may contain lead oxide and is anything but harmless. Although lead would normally not oxidize at these temperatures, friction and the resulting powder may increase the surface ratio so much that oxidation of lead may occur, posing a major health hazard. This black dross must be treated with the utmost care and reference should be made to local environmental and health and labor legislation. Naturally, the use of an inert atmosphere largely eliminates the creation of both types of dross and thus the threat to health.

Another distinction is related to flux, which is applied separately in the wave soldering process. The choice of flux directly impacts solderability issues as well as the resulting cleanliness of the assembly after soldering. There are, however, other issues also related to flux such as costs and potential problems with volatile organic compounds. It is well established that the use of nitrogen generally allows the use of milder fluxes and much lower quantities than would be tolerable in air. It is less understood that residues under nitrogen are less objectionable and, where necessary, easier to clean because they are not oxidized as they are in processes operated under air.

In many cases of wave soldering, the method of flux application is changed from foam fluxing to spray fluxing once the step from ambient soldering to inert soldering is taken. On the one hand, controlling the amount of flux applied to the board during fluxing is essential, as it correlates directly with a decrease in SIR (Surface Insulation Resistance) value after soldering. High SIR values are becoming more and more important as the pitch decreases and particularly with high frequency circuits.

But spray fluxing under nitrogen also has its monetary rewards: savings in flux and alcohol solvents may be dramatic and may directly justify the switch to spray fluxing. Most wave equipment manufacturers recommend as much as a 60% reduction of the flux application when inerting. Various published and unpublished reports have supported flux reductions in spray fluxing when switching from air to inert.

Inerting the wave soldering system may be done in a number of different ways. Systems are available that only protect the solder pot area either with a blanket of nitrogen gas bled over the wave crest (inert boundary). These systems can be retrofitted (figure 2). Such methods enable a significant reduction of dross and provide higher quality while minimizing investment and maintaining low operating costs.

As another option, inerting tunnels are offered in different lengths and designs. It is easier to inert the critical region properly if the interface with the environmental air is pushed as far away as possible. Properly designed and maintained tunnel systems translate to very low dross production than short hoods and inert boundary systems. Capital costs of tunnels are, however, higher than localized inerting systems. Whether it is necessary to seal equipment hermetically remains to be considered.

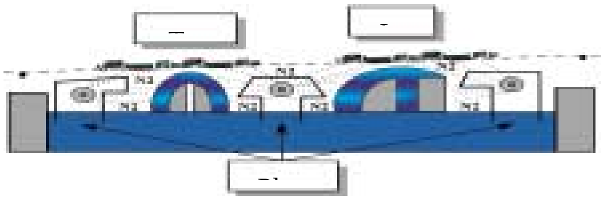

Figure 2: Example of Inert Boundary System

NITROGEN AND REFLOW

In reflow flux activity, residues and cleanliness also play a major role when deciding whether nitrogen should be used or not. The same arguments apply that have been used in wave soldering: residues are less objectionable and, if necessary, easier to clean because they are not oxidized as they are in processes operated under air. One study[9] even indicates that nitrogen reduces residues for some fluxes as much as 66% (depending on the specific paste) compared to their application in air. This explains why many users switching from ambient atmosphere to nitrogen notice a reduction of the incidence of failure of the needle-test itself. Failure of the needle-test depends on the amounts of deposited residues and the stickiness of the rosin.

The most important factor in considering a nitrogen process is quality defined in terms of defect levels and reliability of the joint. Longitudinal studies[10] have provided enough reliable data to confirm that both of these important factors are positively affected by the use of nitrogen. In large-scale manufacturing situations, defect levels were monitored over a two-year period, one year prior to a switch to nitrogen reflow and one year after the switch was completed. With the introduction of nitrogen as the only significant change, the defect level fell from 82 to 37 dpm, a decrease of more than half.

Other operations[11] where nitrogen was introduced have shown improvements in First Pass Yield between 5 and 7%, which translates into a reduction in defect levels of between 50 to 60 percent. The fact that not every introduction of nitrogen was equally successful is explained by differences in layout and pitch. Admittedly, bad layout cannot be compensated by just the introduction of nitrogen as a cover gas. On the other hand, it seems that those processes with the narrowest pitch benefit the most from use of nitrogen. In other words, the narrower the pitch, the more one can gain by recommending nitrogen for the process.

LEAD-FREE SOLDERING

After a certain amount of anxiety caused by legislation before the US Congress and Senate in 1995, the question of lead-free soldering had become a non-issue until a push by the Scandinavian Countries introduced a series of drafts on lead waste in the EU. This proposal would effectively ban the use of lead (and some other materials) for European companies. With heavy support from Japan and some cautious reactions in the US, lead has become once more a major point of concern and discussion.

The problem of soldering without lead is an intricate one. Many different aspects play into it: toxicity, availability, price, worldwide distribution, wetting ability, reliability, and many more.

Much effort has gone into finding a replacement for 63/37, not only because of its lead contents (most specialists agree that the danger posed by lead in the solder is rather limited) but because there is a general need for a ‘better’ solder. However, so far nobody seems to have been successful in finding just that ideal combination that replaces (as a drop-in) the solder of 5,000 years ago.

The few potential choices (tin plus some copper; tin plus some silver; tin plus some copper <u>and</u> some silver, etc.) all need higher process temperatures and thus may not really work without good inerting[12]. The increased amount of tin in the solder not only makes them somewhat more expensive (lead is cheap!) but heightens the tendency to oxidize, dross and to react with other metals. Although the higher tin content would lead one to believe that wetting could be improved, this is not generally true. Only under nitrogen do we generally achieve similar wetting as for the eutectic tin/lead composition.

The question of inerting becomes even more critical when other solders are considered: indium, zinc, bismuth and antimony are just some elements that may be found in our solders in the future. Most such solders show very bad wetting properties in air and some of them are even marginal under nitrogen. And the *CERCLA Priority List of Hazardous Substances* reveals that some of the reaction products of these metals may actually pose a greater threat to an employee’s health than lead. Whether nitrogen can help in this regard must be studied in great detail[13].

CONCLUSION

The use of nitrogen in flow and reflow equipment may benefit the process, as well as the quality of the end product. In both cases, reliability of the joint may increase (perhaps the amount depending on the type of base metal used) and defect levels may drop to improve the First Pass Yield. In the case of wave soldering, other benefits may accrue such as dross reduction, reduced solder pot maintenance, a safer operation, and substantial savings of flux.

A nitrogen process should, however, not be adopted without fully understanding its benefits and limitations. Nitrogen opens the process window by forgiving the process flaws, but is the increased window necessary? As the pressure to reduce cost in the industry is continuously increasing, the ultimate decision to use nitrogen should be based on a solid cost-vs.-benefit analysis which goes beyond the unit cost of nitrogen itself. Testing is recommended for that purpose. Nitrogen is inevitably an added cost to the process, but its overall benefits normally should outweigh the additional expense for a user to adopt it.

Despite a continuous improvement in flux chemistries, nitrogen is here to stay and its usage will increase in the industry. The continuous integration of components, the increased demand for higher quality and reliability assemblies, as well the introduction of lead-free solder all increase the vulnerability of the process to oxygen and oxides, enhancing the value of inert soldering.

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