SOLDERING IN A NITROGEN ATMOSPHERE

INTRODUCTION.

Oxygen is a wonderful gas. Without it we would all be dead. Oxygen combines with all manner of things and the world is a better place for it; most of the time we should leap and whoop and dance with arms and legs and proclaim in a great voice, 'Hooray for Oxygen!'

But sometimes oxygen gets in the way.

Oxygen and many metals have a great affinity for either other. (If you don't believe me, try leaving an expensive steel wrench out in the dews and damps for a while. Many people blame the water, but it's really the oxygen.) Soldering involves metals: the wires are metal; the bits on the board, if we are soldering to a board, are metal; and of course the solder itself is metal.

You don't really want a lot of oxygen around when soldering. Oxygen and metals form metallic oxides; oxides form much more rapidly in a hot atmosphere (and soldering is a hot process); these oxides shield the conductors from either other, keep the solder from adhering to what metal is left, and are no help.

Flux will eat away the oxides — that's its job. But when the flux is gone and its residues are washed away, here comes the oxygen again, bringing flowers and candy and anxious to get together -

Obviously it would be a Good Thing to keep the oxygen away. Flooding the soldering area with an inert gas is one way but we should be judicious about it. Inert gases, or noble gases, abound. They are relatively costly. Nitrogen abounds too - almost 4/5 of the atmosphere is nitrogen - and nitrogen, though far from inert, reacts slowly with metals. More, it is relatively cheap.

Flux + chemical residues + allerverdammter Verstünk (a damnable stink)

The use of nitrogen to render the atmosphere chemically inert whilst soldering has become a rather common practice. It is widely accepted in the electronic assembly industry that nitrogen 'improves' the wave soldering process; however, its use in reflow equipment is much less frequent, and often questioned. In point of fact, though, hot nitrogen rework tools were introduced at almost the same time as the first nitrogen atmosphere wave soldering equipment.

This insecurity about the benefits of nitrogen certainly does not stem from a lack of information and research. The literature is full of indications about the hows and whys of nitrogen usage - applied to wave as well as to reflow soldering - so that 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 what its limitations are.

WHY USE NITROGEN?

There are general trends that favor the use of nitrogen. The miniaturization of components and the development of high-density components & the search for a superior surface finish on PCBs - the lure of image. Fine pitch components demand better planarity conditions than HASL, with its awkward meniscus, 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 enters into the surface issue. The complexity of the modern assembly is not only reflected in the number of layers of the board but also by the pressing need for multiple soldering processes or clever process modifications such as reflow soldering through whole components.

It seems that Organic Solderability Protection (OSP) - 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.

The question of the reliability of the soldered joint was underlined by Potier and Conor. In a project supported by the German government, stress experiments yielded some unexpected results. Failure patterns in a component A and a component B (different vendor) 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 somewhat better for component B: 302:100.

Such findings are corroborated by other research in which the peel strength of joints was examined, again showing an advantage for those joints soldered under nitrogen. A similar study performed at Siemens seconds those findings.

WAVE SOLDERING USING NITROGEN.

Nitrogen soldering was commercially introduced in Europe and first made its in-roads there, although experiments with nitrogen equipment were done very early in North America as well as in Europe. Different types of equipment have been made available, reflecting the different motivators for its use. The fact that the wave (or the flow) soldering process is distinctly different from the reflow process, adds a few points that must be considered.

Paramount among those is the creation of dross. 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 other 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. One computer manufacturer facility converted all of its wave machines to nitrogen after one of its wave maintenance technicians was apparently diagnosed with lead poisoning. Naturally, the use of an inert atmosphere largely eliminates the creation of both types of dross and thus the threat to health.

One essential point is related to flux, which is applied separately in the flow 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 a problem with volatile organic compounds as well as costs. That the use of nitrogen generally allows the use of milder fluxes than would be tolerable in air is a well-established fact. Less known may be that residues are less objectionable and, if necessary, easier to clean because they are not oxidized as they are in processes operated under air.

In many cases, 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 value. High SIR values become more and more important as the pitch decreases, particularly in cases in which high frequency circuits are involved.

But spray fluxing under nitrogen also has its monetary rewards: savings in flux and alcohol solvents may be dramatic and may justify the switch to spray fluxing. There is also the accompanying problem of flux and alcohol handling and storage. One TI facility reported flux usage reductions from 600 gals (2271 liters) RMA to 12 gals (45 liters) LR, and alcohol dropped from 2000 gal (7571 liters) to 0.

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) or with a hood. These systems can be retrofitted. Such methods enable a significant reduction of dross and provide higher quality while minimizing investment and maintaining low operating costs. The best of these systems should offer 10 ppm at the board, 80 percent dross reduction and a nitrogen flow of 300 scfh (8 Nm^3/h) per wave.

Tunnel designs of different length and different conception are being offered. It is easier to inert the critical region properly if the interface with the environmental air is pushed as far away as possible. Nitrogen consumption rates differ greatly, depending on design, length of tunnel and required ROL values. Properly designed and maintained tunnel systems should show nitrogen usage rates of 750 to 1200 scfh (20 to 30 m^3/h) when ROL values of 20 to 50 ppm are targeted. These figures also translate to lower dross productions (90 to 95 percent) than short hoods and inert boundary systems. Capital costs of tunnels is, however, higher than localized inerting systems.

Whether it is necessary to seal equipment hermetically remains to be considered. The cost of equipment and the difficulty of access may outweigh the benefits.

NITROGEN AND REFLOW.

In reflow, flux activity, residues, and cleanliness are significant when deciding whether nitrogen should be used, and the same arguments obtain that have been used in wave soldering. Build quality, with reference to number of defects and reliability of the joint, is of paramount importance. Longitudinal studies provide enough reliable data to confirm that all these important factors are improved by the use of nitrogen. In large scale manufacturing situations, rework defects were monitored over a two-year period, i.e. one year prior to a switch to nitrogen reflow and one year after the switch was completed. With the introduction of nitrogen being the only significant change, the proportion of defective joints fell from 82 to 37 dpm, a decrease of nearly half.

Other operations have shown improvements in First Pass Yield from five to seven percent, which translates into a reduction in defect levels of 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 for only by the introduction of nitrogen as a cover gas. On the other hand, it seems that those processes benefit the most that have the narrower pitch. In other words, the narrower the pitch, the more one has to recommend nitrogen for the process.

Whereas ROLs in wave soldering should be in the range of 20 ppm or lower to achieve best performance, the values for reflow seem not to be as critical. All the indications are that ROLs of <500 ppm in the peak zone are sufficient to reap the full benefits of inerting, with values between 500 and 1000 ppm for the rest of the equipment, where the temperatures are lower. These less demanding values are explained by the fact that most of the metal is covered either by paste or does not see the same high temperatures as in flow soldering operations. Since most of today's equipment has been designed to offer lower ROLs at reasonable consumption rates [<1500 scfh (40 m^3/h)], it may be safe to operate the peak zone below 100 ppm ROL.

EFFECTS OF NITROGEN.

In soldering, there are a number of basic phenomena caused by changing the ambient gas (air) to nitrogen. Let us first examine these and then see how they, in turn, may translate into some interesting benefits for the different processes.

Research examining the spreading behavior of solder under different environmental conditions shows that spreading starts at lower temperatures as we reduce the Residual Oxygen Level (ROL). In Dong 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, indicating an inhibiting property of oxides to the tendency of spreading.

Earlier research had asked a similar question directed at the coverage of copper under atmospheres of different quality and came to a parallel conclusion. Good copper coverage by liquid solder is achieved only at low ROL (<40 ppm).

In the presence of flux, we have a similar situation. Warwick found when investigating fluxes with varying amounts of non-volatile (NV) matter that dewetting occurs in air for fluxes with low amounts (<50percent) of NV matter, whereas no dewetting was recorded for the same experiment performed under nitrogen. Even very low levels (20 percent) of NV matter in the flux did not result in any dewetting.

Related to this question is the parameter known in the industry under the name 'wetting force.' Usually measured with a wetting balance, it is an indicator for the quality and shape of the joint. A somewhat puzzling result has been recorded here, which may perhaps be best understood 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. Those that have deteriorated solderability, however, 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 it is 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. For the applied process, this means that if all the boards and components always have excellent solderability, then nitrogen does not help with the set of 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.

Comparing wetting force for different fluxes in air and nitrogen again yields results indicating that nitrogen coverage can improve the process. Adams, et al compared a number of fluxes and found that with a notable exception (adipic acid), the wetting force is even higher for fluxes if measured under nitrogen rather than air. For some of them, the gain is substantial.

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

The surface tension of the liquid solder is important 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 contend with those measurements available to us, where a minute amount of tin oxide in the surface layer will falsify the measurement. Nevertheless, these measurements 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 solved. The tin oxide in the boundary layer may cause this difference in measurement. For practical applications, it is not the theoretical values but the values that reflect the actual situation that are the most important. For the process, this means that surface tension will be lower under air than under nitrogen.
An excellent demonstration of higher surface tension is verified by an experiment carried out by Dong. 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 also aided.

The same article also investigated the dependency of oxygen depravation and metal powder particle sizes in pastes. The tendency towards fine pitch and the consequent use of paste with finer grain sizes stresses the importance of such questions. Not only did the experiment confirm that nitrogen coverage improves solder spread in all cases, but it also has shown that the finer the powder size, the more important will be the use of an inert cover gas to achieve sufficient solder spread.

The prevalent oxide found on 63/37 molten solder is SnO. Other solders may contain indium oxides or zinc oxides. Experience has shown that such oxides can be rather troublesome during the soldering process and efforts have been directed at the reduction of such oxides. One of the benefits of inerting may be the fact that such oxides start to dissolve at relatively low temperatures, when no oxygen is present. Depending on the solder composition, the oxide layer may increase in air over time rather quickly (e.g. with 63/37 solder) or slow down dramatically over time (e.g. in the presence of silver of copper). In any case, dissolution of SnO has been shown to start under good nitrogen coverage only 10K or 15K above the melting point for silver and copper-bearing solders. Even 63/37 solder shows dissolution of oxides starting at 500°F (260°C) under nitrogen atmospheres.

NITROGEN.

Nitrogen makes up about 78 percent of the air; 20% is oxygen; whilst the rest consists of CO; CO_2; a few of the 'noble' gases, primarily argon; and a soupçon of still other gases. Nitrogen in and of itself is not toxic, but of course it cannot sustain earthly life, which is based upon a carbon-oxygen cycle. It is advisable, then, to avoid flooding the area with pure nitrogen if the gas is to be used in an industrial process. People can always find ways to do foolish things.

Nitrogen boils at about -320.4°F (-195.8°C) (normal pressure), so 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 given a chance.

The absence of oxygen in pure nitrogen and the fact that it does not readily react with common metals has earned it the designation 'inert.' It is this property that is used when soldering to protect metal surfaces from oxidation during heat-up and to assure proper action of flux.

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 and perhaps best-known one is a 'freezing' process, usually referred to as 'cryogenic.' A cooling process is used to liquefy the gas, which in a kind of reversed distillation process purifies itself because of the different boiling points of oxygen and nitrogen. More recent 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 95.0 to 99.99999 percent [=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 (<500 ppm), only liquid nitrogen (cryogenic purity) or Liquid-Assist on-site systems (cryogenic purity) are recommended for assembly operations.

SUMMARY.

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 (the amount of increase may depend on the type of base metal used) and defect levels drop to improve the First Pass Yield. In the case of wave soldering, other benefits may accrue such as dross reduction and reduced solder pot maintenance, a safer operation and, substantial savings of flux.