To what extent should there be concern about ionic residues remaining on an electronic circuit assembly? Graham Naisbitt, GEN3 SYSTEMS

Fact 1:

All fluxes leave residues.

Fact 2:

Manufacturers of "No-Clean" fluxes fully understand Fact 1.

Fact 3:

There are many circuit assemblies that work reliably with neither cleaning nor conformal coating involved in the assembly process.*

Trying to determine whether process residues, especially flux, might compromise circuit performance, from an electro-chemical stand-point, can only sensibly be done using measurements of SIR (Surface Insulation Resistance). Unlike other test methods, SIR testing does not discriminate between ionic and non-ionic contamination.

Other techniques, FTIR – Ion Chromatography – Ionic Contamination Testing, are all very effective at measuring the presence of ionic salts that have been brought into solution. They are **not** however capable of determining whether their presence will compromise circuit reliability.

In the case of lonic Contamination testing, like any de-ionised solution, it is hungry for ions and will aggressively seek them out. Unlike lon Chromatography, it is **not** able to discriminate between individual ionic salts: Bromine, Chlorine etc., but its original and primary purpose is to control the assembly process. It's purpose is **not** to dissolve all process residues, notably fluxes, and attempts to use it this way yields both false positives and false negatives, as well as time consuming argument and frustration.

* A caveat to Fact 3 is that continuing miniaturisation and increasing packaging density are, perhaps, arriving at the frontier of reliability, hence the undisputed fact that more and more manufacturers are returning to cleaning.)

The question is, therefore, "How clean should an assembly be to be functionally good?"

Electronic circuit assemblies are the result of at least 30 different chemical processes, residues of which, when combined with moisture and electrical current will destroy electronic circuits by electrolysis.

Clearly, therefore, care needs to be taken to minimise the risk of electrolysis. This condition requires 3 fundamental ingredients: Humidity – Ions (AKA Salts) – Electrical Bias. Remove any one of these three elements, and this problem won't occur. (See Figure 1)

The operating circumstances for the end product have a direct influence on the time it might take for this electro-chemical reaction to occur hence, at least in part, the classifications employed in IPC-J-STD-001:

Class 1 = General Electronic Products Class 2 = Dedicated Service Electronic Products Class 3 = High Performance Electronic Products

It is easy to understand why the reliability of a mobile phone (Class 1) is of far less consequence than that of a business server (Class 2) or the air bag on your car (Class 3).



Figure 1 Venn Diagram



Controlling the circuit's operating environment and identifying the influence ionic residues presents a difficult, but not insurmountable, challenge.

This challenge applies to the design, production, process and quality control engineer.



Figure 2 Courtesy of Harvard Business School (Business Week Magazine)

\$100.000

\$10,000

- Design for Reliability
- Characterise the Production Process
- Control the Process
- Produce Quality
- Increase Profit

Establishing and maintaining the quality of the product whilst meeting the design criteria certainly has a direct influence on the profitability of the end product. (See Figure 2)

Clearly the circuit manufacturer has to balance the issues of warranties, product safety and the consequential losses of product failure.

Unfortunately ionic residue levels have, in themselves, become confused in many minds as a criterion of "goodness" or "badness" of the product. The ultimate test is surely one of performance rather than the measured ionic contamination level.

\$1,000,000

Since the mid-1990's the industry has, in the majority, adopted a "no-clean" process. Clearly, not cleaning assemblies that have been subjected to so many chemical processes, demands considerable control of the overall process. Refer to Fact 1.

"No Clean" Fluxes are composed largely of weakly-ionized organic acids at low solids levels which, at soldering temperatures, are sufficiently active to provide good cleaning of the metallic surfaces and wetting by the molten solder. In most instances, much of the organic acid is volatilised at the soldering temperatures or neutralised by chemical reaction. Some traces of the organic acids, however, are always present after the soldering.¹

The final product will, presumably, have been tested to establish its fitness for purpose. What concerns us here is either the extent to which it is necessary to remove these residues, or the understanding of whether such residues are safe to be left behind.

How can this be measured?

Cost

\$1.000

- Surface Insulation Resistance testing will inform if the circuit will be electro-chemically reliable. It will not inform what is present that is causing a failure.
- Ion Chromatography and FTIR will identify exactly what is present on the sample being tested, but it will not inform as to whether the end product will be reliable.

It may, very possibly, be necessary to have the results from both tests – SIR then IC or FTIR to establish what was present causing the SIR issue.

The electro-chemical sensitivity of a circuit is best measured by the use of Surface Insulation Resistance testing. All process materials, including solder resists, liquid solder flux, solder paste, conformal coatings etc., are required to be tested for their individual SIR values: IPC-TM-650 2.6.3.7



However, understanding how each material might react in the presence of other process materials is now the most important requirement as circuits have become far smaller and are subjected to increasingly hostile operating environments.

Process Characterisation Testing, using either IPC 9202 or IEC 61189-5-5, set out the requirements to characterise any given production process material set, from an electro-chemical standpoint. From such testing, acceptable levels of ionic contamination can be determined that may be used to control the assembly process on each individual production line.

Process lonic Contamination Testing – otherwise referred to as PICT (aka ROSE) testing, is ideally suited to this role. However, its purpose is **not** to dissolve all ionic residues, rather, it is to identify whether those residues that are most easily brought into solution fall within acceptable pre-determined levels. It should be used to periodically check the process and, quickly and accurately, identify any increases of ionic levels beyond those pre-determined levels.

This test method has been around for almost 40 years. It employs a mixture of alcohol (Iso-PropanOI) and deionised water that is "polished" via an ion exchange column to a Resistivity level of better than $20M\Omega$

Amounts of ionic materials in the test solution are expressed by a conductivity factor that is equivalent to the measured conductivity contributed by a known amount of a standard, strongly ionized salt such as sodium chloride (NaCl). Ionic residues are therefore usually expressed as equivalents of sodium chloride

in micrograms per unit surface area (x μ g/cm² \equiv NaCl) of the sample. This does not imply that the contamination is NaCl, but that it exhibits conductivity equivalent to that of the expressed amount of NaCl if it were in solution instead of the ionic soil.

When an ionic contaminant comes into contact with water, this conductivity value will increase due to the dissolution of the contaminant into the water. If the surface area and the type of contamination are also known it is possible to express the amount of contamination present, as a given weight per unit area of board.

The addition of a strongly ionized salt to deionized water will enhance its electrical conductance to a degree that is nearly proportional to the concentration of the salt. Conductance measurement can thus be used to indicate concentration of an ionic salt extracted into a solution.

This de-ionised test solution is extremely aggressive and becomes even more so if heated. In work originally conducted by Swedish Group IVF, on behalf of The European Space Agency,² it was found that prolonging the circuit's exposure to this solution actually led to the leaching of the Bromine flame

What is an lon?

An ion is an atom or molecule in which the total number of electrons is not equal to the total number of protons, giving the atom a net positive or negative electrical charge.

lons can be created by both chemical and physical means. In chemical terms, if a neutral atom loses one or more electrons, it has a net positive charge and is known as a cation. If an atom gains electrons, it has a net negative charge and is known as an anion.

lonic bonding is a kind of chemical bonding that arises from the mutual attraction of oppositely charged ions. lons of like charge repel each other, and ions of opposite charge attract each other. Therefore ions do not usually exist on their own, but will bind with ions of opposite charge to form a crystal lattice. The resulting compound is called an **ionic compound**, and is said to be held together by ionic bonding. In ionic compounds there arise characteristic distances between ion neighbours from which the spatial extension and the ionic radius of individual ions may be derived.

The most common type of ionic bonding is seen in compounds of metals and non-metals (except noble gases, which rarely form chemical compounds). Metals are characterized by having a small number of electrons in excess of a stable, closed-shell electronic configuration. As such, they have the tendency to lose these extra electrons in order to attain a stable configuration. This property is known as electropositivity.

Non-metals, on the other hand, are characterized by having an electron configuration just a few electrons short of a stable configuration. As such, they have the tendency to gain more electrons in order to achieve a stable configuration. This tendency is known as electronegativity. When a highly electropositive metal is combined with a highly electronegative non-metal, the extra electrons from the metal atoms are transferred to the electron-deficient nonmetal atoms. This reaction produces metal cations and nonmetal anions, which are attracted to each other to form a **salt**.

(Thanks Wikipaedia)



retardant out of the board laminate, through the solder resist / mask and onto the board surface. However this is ionic material that would be both necessary, and safe, to leave present.

For this reason, there should be a time limit for this test, typically <15 minutes and at a controlled temperature level.

From the process engineering stand-point, the shorter the test time the better. This might be less significant If the production volume is low, but if production is measured in hundreds of circuits per hour, the financial department will become stressed and, in turn, so will production as the business ships product that falls outside the quality control standards, and rework or replacement becomes necessary.

The test should not be run over an extended period of time in a futile attempt to dissolve and bring into measurable contact all ionic matter. As explained earlier, many, if not all, of such residues may actually be desirable.

There are 2 types of test presently available: Static and Dynamic.

As a reminder, the **sole** purpose of this test is to control the assembly process from detected changes of resistivity / conductivity that might exceed pre-established limits.

Static Testing is a **Closed-Loop Test.**

Here the test solution is polished to a conductivity level of better than $20M\Omega$. The specific gravity and temperature of the test solution are recorded, and the sample is inserted. The polishing resin column is taken out of circuit. The test solution is re-circulated past the conductivity sensor and the conductivity values before and after the test show the amount of ionic matter that has been brought into solution.

Dynamic Testing is an **Open-Loop Test**.

This method is more akin to a cleaning process, which is not the objective. As with the Closed-Loop Test, the test solution is polished to a conductivity level of better than $20M\Omega$. The specific gravity and temperature of the test solution are recorded, and the sample is inserted. The test solution is then re-circulated past the conductivity sensor and directly through a polishing resin column and the accumulated ionic contamination measured. The test time may be extended to 1 hour and attention must be given to the test solution temperature during this time.

Additional Considerations:

1. Do electro-chemical reactions apply in the case of AC, high frequency circuits?

It is thought that these electro-chemical influences are less relevant with AC circuits than DC circuits. However in a DC circuit the electrons migrate down the centre of the conductor, whereas, in a high frequency AC circuit the electrons migrate to the periphery of the conductor – and that's where much of the process residues reside...and that is why even high frequency circuits suffer from electro-chemical reactions: dendrites and periodic, if not premature, failure.

2. Might the use of a conformal coating overcome such electro-chemical issues?

There are many who might apply a conformal coating as an attempt to avoid the electrolysis issue. However, as all coatings breathe, the presence of any ionic matter can initiate an osmotic reaction. Osmosis is where moisture-laden air passes in and out of a coating film attracted by the presence of ionic salts. The salt swells, as the moisture dissolves the salt, inducing pressure that may be extreme. In the case of zinc, this is >200Bar!

3. Will cleaning a no-clean present any problems?

We know, today, that is not merely the presence or absence of ions, as such, that determines good or bad behaviour of a material residue. Some of the poorest electrical behaviour experienced has been seen with surfaces that had been contaminated with polyglycols and polyglycol surfactants.



These materials, although completely non-ionic, may, nevertheless, have disastrous effects on SIR and Electro-Chemical Migration if they are residual on the laminate surface. Such materials are commonly used in various process materials including solder resists / masks, solder levelling fluxes as well as no-clean solder fluxes whether in liquid or paste form.

4. Why should no-clean present more problems?

In the past, when rosin based fluxes were in common use, the solids content (i.e. the ratio of rosin to the liquid / solvent carrier) was usually in the range of 15% to 30%. Modern no-clean formulations however, have typically 0% to 2% solids.

If these fluxes were a ceiling paint, then you too would be curious to know how you get 0% to 2% solids paint (or in this case flux) to stick? The use of these polyglycol / surfactant "wetting" agents deals with this particular issue. However, all of this excess liquid demands that higher process temperatures be employed and a higher temperature leads to greater absorption into the surface of the plastic laminate. Now add in the higher temperatures required for a lead-free process, and it can be seen that this issue will be exacerbated. These residues are exceedingly difficult to remove and they will give serious degradation of the subsequent measured values of SIR.

5. What is the likely impact of contamination from production processes on the reliability of printed board assemblies?

"J-STD-001 divides electronic assemblies into three end- product classes depending on end-item use, which seems reasonable. Nevertheless, the requirement regarding ionic residues is the same, regardless of product class, which does not appear reasonable. Ionic contamination will have negligible effects on the reliability of electronics used in dry environments, whereas they cause failures within a very short time if water is condensed on the surface of unprotected biased PBAs.

Another drawback with the method used for ionic residue measurements is that it does not distinguish between different ionic contaminants. Others [sic] have shown that various ionic substances have very different impact on the surface insulation resistance. Furthermore, they observed a strong synergistic effect when they combined a rather harmless ionic substance (adipic acid) with an organic non-ionic but hygroscopic substance (polyethylene glycol). In fact, they got the same effect as with sodium chloride. These results pinpoint the main problem with cleanliness evaluations based on measurements of contamination levels. Such cleanliness measurements do not constitute reliability tests. If the results shall be of any value, there must be a clear known relationship between the measured parameter and the effect it has on reliability. Since various substances have different effects on the reliability, there should be an acceptance requirement for each specific substance. Furthermore, possible synergistic effects must also be considered. It is evident that this is not a feasible way to deal with cleanliness requirements. Instead of measuring what is on the assemblies, a method for cleanliness measurement should be based on measuring the effect of contaminants on the reliability. One such method is surface insulation resistance (SIR) measurements."

6. How difficult is to dissolve ionic contaminants? "One possible explanation for the slow dissolution of the ionic contamination is the sponge-like epoxy surface of an FR-4 board (Figure 3) which makes it difficult to dissolve contamination at the bottom of the depressions.

However, of greater importance for the observed results probably is the fact that flux residues are absorbed into the laminate. It has been known for a long time that polyglycol materials are absorbed in the epoxy resin of FR-4 laminates and that it is very difficult to remove these residues by cleaning. There also is evidence that inorganic ionic compounds may be absorbed into polymeric



Figure 3 Scanning Electron Micrograph of the surface of epoxy resin in an FR4 laminate



materials. Sanftleben has shown that high concentrations of chloride from fluxes used for HASL are absorbed into solder masks, and that these residues are impossible to remove completely, even if very efficient cleaning processes are used. There also are indications that halides are absorbed into the epoxy resin in FR-4 laminates. Since the boards are heated to temperatures above 200°C during the HASL process, far above the glass transition temperature (Tg) for the epoxy, the epoxy is soft at these temperatures and low molecular weight substances can diffuse into the epoxy matrix.

If contaminants are absorbed into the epoxy matrix, it will be impossible to completely remove them and, no matter how well the boards are cleaned, contaminants remaining in the epoxy matrix will always diffuse out onto the surface after some time, especially at high temperatures such as during soldering processes."³

Conclusion:

Establishing the answer to the question: "How clean is clean" is not straightforward. No single answer will suffice; it is finding the ideal balance between the effects of electricity and humidity on a circuit that may be either high or low voltage, high or low frequency and long or short warranty.

In all cases, these tests are both time consuming and expensive, so it is of high importance to employ a control that is fast, accurate and easy to run.

Closed-Loop Process Ionic Contamination Testing – PICT – is an ideal way to control the assembly process, including no-clean. It should be used in conjunction with the other test methods having first established the desired performance criteria using Surface Insulation Resistance Testing.

1 Circuit Board Ionic Cleanliness Measurement: What Does It Tell Us? Dr. Jack Brous, Alpha Metals Inc. Jersey City, New Jersey, USA

2 B. D. Dunn and C. G. Bergendahl, An Evaluation of the Solvent Extraction Method for the Detection of Ionic Contamination on Substrates Supporting Large Surface Mounted Devices, Brazing & Soldering, No. 13, pp. 20- 27 and 32, 1987.

3 Impact Of Contamination From Production Processes On The Reliability Of Printed Board Assemblies* Dr Per-Erik Tegehall IVF - The Swedish Institute of Production Engineering Research, Argongatan 30, SE-431 53 MoIndal, Sweden

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