# Cleaning PWAs in Electronics by Inventec Performance Chemicals

# The Greenway of Understanding Today's Cleaning's Needs

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## Introduction

The electronic market pushes the electronic manufacturers to add more functionalities and to miniaturize the electronic printed wire assemblies (PWAs) to improve their connectivity for the automotive, aeronautic, military and medical devices. As a follow-up of the paper written in 2011, "Cleaning Electronics: understanding Today's needs" (Ref[1]) and in 2017 "Optimization of chemistry for vapor phase process to de-flux no clean lead-free materials on PWAs" (Ref[2]), it has been demonstrated the segregated Bi co-solvent vapor cleaning process is performing the best to match today's miniaturized electronics' specifications.

To achieve a good cleaning result, it is worth understanding the key parameters present and the physical laws which are ruling this chemical operation.

Following of the ban of CFC's, HCFC's and brominated solvents, standard solder pastes and fluxes evolved from RA and RMA fluxes, to No-Clean, to low residue No-Clean, fully synthetic, to very low residue No-Clean and to water soluble No-Clean. Moreover, the electronic assembly industry did substitute in many applications the leaded alloys by lead-free ones as tin-silver-copper. Many companies came out with their cleaning solutions, aqueous, semi-aqueous and solvent based, with each product release being more innovative than the previous one. Unfortunately for most of the cleaning suppliers, two other trends appeared: lead-free soldering and the aggressive miniaturization of electronic devices.

Past chemicals like CFC's, HCFC's, brominated solvents, detergents and glycols cannot do a good cleaning job anymore because most flux formulations have changed. Cleaning has a cost and it should be adapted to the needs while maintaining stability, efficiency, quality, reliability and performance. Thus, it is important to remember that the world is composed of two main families of products: organics and inorganics. 2020's regulations request stricter involvement by the companies for the worker's safety and the environment, like non-hazardous chemicals, recyclable, sustainable cleaning solutions and energy saving.

Cleaning performance is affected by three main key parameters:

- The first involves the solvency power of a product which is sometimes measured by the Kauri Butanol Index (KB Index). Detergents are not related to the KB Index, but rather to the detergency power which will not be discussed here.

- The second is surface tension, expressed in mN/m. These parameters must be considered because when the cleaner cannot make contact with the contaminants under or around components, the contaminants cannot be dissolved.

- The third point is composed of physical parameters like temperature, mechanical activities, and the duration of the process.

Finally, the usual methods of control, contaminometers/Ionograph, SIR are facing some credibility issues because of this miniaturization and the very low stand-off met today. Typically, some high residue flux concentrations remaining underneath a compact/low stand-off component. Or even cleaner' residues? For these reasons, the IPC Norm TM650-2.3.28b was developed. It is a test procedure designed to measure the level of extractable ionic contamination on the surface of a printed circuit board by ion chromatography. This method requests an ion chromatography analysis on/under components to extract any local residues below and around components. Actually, these analyses were run by a worldwide known manufacturer with additional methods as C3 Surface ion extraction (CI) and the solutions analyses like conductivity (CM), followed by the ion chromatography (IC).

The purpose of this study is to benchmark Inventec's segregated Bi co-solvent vapor cleaning process versus an in-line aqueous cleaning process used by a military PWAs manufacturer and to compare the results.
Inventec's knowhow manages all these parameters while facing high-tech miniaturization and environmental care, like ROHS, REACH, etc. and brings innovative cleaning solutions, Greenway® lines in this electronic world, matching by far the existing solutions.

## 1) Miniaturization

Miniaturization and reliability are essentials. Today, size of components is down to 0.1mm (<0.5 Mils) and lower stand-off can be between 250µm and 400nm. The reliability of these components should be always increased. This miniaturization should not become a reason of instability and unreliability. The cleanliness should be achieved and pass new level of specs. **Figure 1: Transistor size projection**

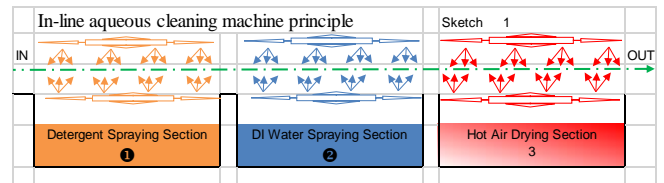

Figure 1: Transistor size projection
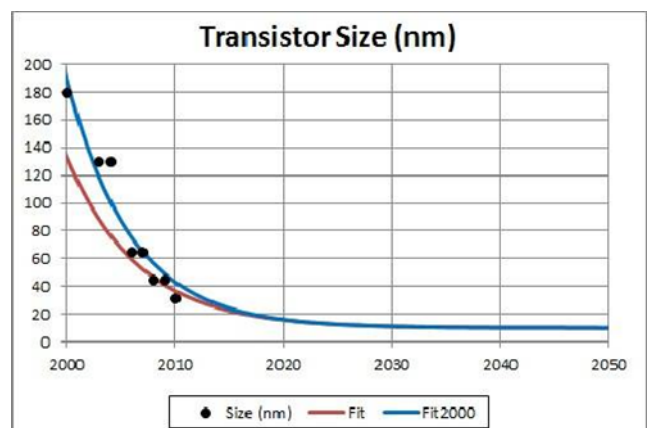
## 2) Contaminants

The contaminants on a circuit board are mainly composed of organics such as natural and/or synthetic rosins, acids, fingerprints and inorganics as, ions, solder balls, water soluble residues and particles of PCBs. The lead-free alloys need higher soldering temperatures than the standard Sn/Pb which are inducing significant evolutions on the fluxes. These fluxes are most of the time more active and must resist higher reflow temperature profiles. They present more risks than the one formerly used, and the temptation is high to choose production parameters allowing shining soldering joints. The ionic cleaning of the PWAs is then more critical before tropicalization coating but will also help to control the assembling process and help to establish final assembly lifetime. The ionic contamination, SIR and the Ion Chromatography controls combined, will provide the best quality indicator for the long-term reliability in the miniaturizing electronic world.
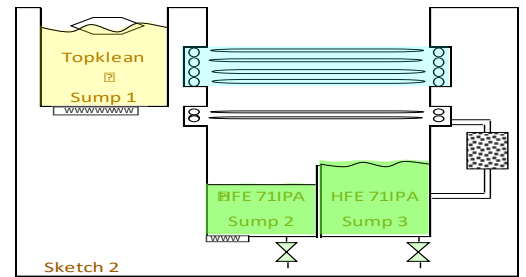
## 3) Cleaning trials set up

Evaluation of a Segregated Bi-co-solvent vapor degreaser versus an in line aqueous cleaning process.

a) The production in-line aqueous cleaning process is using a detergents mixed with tap water to de-flux PWAs in section 1. PWAs are introduced from the left to the right. High pressure jets are used in section 1 and 2 at a temperature of 80°C. Section 2 is using DI water to rinse residues, before hot air drying, section 3. The total cleaning cycle is around 15 Min, belt speed about 50cm/Min. **Please see sketch 1: In-line aqueous cleaning process 1.**



b) The segregated Bi-co-solvent vapor degreaser tested, is a batch system, which is composed of 3 sumps. The sump 1 is filled with a hydrocarbon-based formulation to dissolve flux residues at a temperature of 45°C, with manual agitations. For enhanced efficiency, spray under immersion or else could be used. PWAs were dipped for 10 Minutes in the co-solvent in sump 1, then rinsed in the vapor degreaser with a hydrofluroether azeotrope for 1 Min in sump 2 and 2 Min in sump 3; to be comparable to the aqueous cleaning cycle, here a total of 14Min. **Please see sketch 2; Segregated Bi-co-solvent vapor degreaser process 2.**



c) Four military PWAs produced with no clean solder paste were manufactured. Two of them, 1 and 2 were cleaned with the production in-line aqueous cleaning machine and marked with a red dot. PWAs 3 & 4, were unmarked and cleaned with the segregated Bi- co-solvent vapor degreaser. Components A, B, C are targeted as C3 surface ionic extraction and solutions analysis. Sampling at position: A= U9, 20P QFN, B= U18 8P SOIC, C= U10 8P SOIC.



**Please see Picture 1**

## 4) Specifications set up

Every end-user has their own typical specifications which are dependent on their requirements or the requirements of the customers. For this study, the specifications have been taken as described in Table 1. All residues must disappear, including the contaminants under the components, fingerprints, particle or dust should not remain, including residues of cleaning products. The components, rosins, the underfill and the substrate should not be damaged by the cleaning operation. The parts should be dried at the end of the wash cycle and the ink markings should be resistant to the cleaners. Versus previous papers dated of 2011 and 2017, ionic contaminometers were not used because they are facing some credibility issues caused by this miniaturization. Thus, C3 Surface ionic extraction (CI), Solution Analysis as conductivity (CM), Ionic Chromatography (IC) using C3 extracted solutions, and Optical control with a Microscope were used for this paper (OP).

### Table 1 : Specifications of control

| Method of control | Units |
|---|---|
| OP: Optical IPC-A-610-D | Microscope    5-40x |
| CI: Corrosivity Index. It is the time of max current on C3 running test: Vapor steam surface ions extraction. | Index |
| CM: Conductivity | µS |
| IC: Ionic Chromatography, IPC Norm TM 650-2.3.28b | Total inorganic anions in µg/in.sq |

## 5) Cleaning products availability

As developed in the previous documents, the most important part of the job is to remember which chemical families are available in the market. The cleaning products available can be classified in five different families: The detergents, the light petroleum distillates, Formulated hydrocarbons, Brominated solvents, Glycols and Fluorinated solvents. (Table 2). Only two of them are considered for this trial and thus will be further described.

### a) The detergents: aqueous process 1

Detergents are good most of the time, but very specific to the type of flux residues to be removed. Its concentration is very important in water and can vary between 3 to 50 %wt, in some cases. The temperature can vary from 20-80°C, and the agitation used, sprays, spray under immersion or ultrasonic's should be considered. It is the aqueous cleaning process 1. The drawbacks of these detergents are: the removal of all residues under components because of the poor/high surface tension included between 30-50mN/m, the aggressivity of these formulations and its compatibility with materials, the rinsing with tap or DI water (high surface tension 70-80mN/m), the drying operation, the water-proof compatibility on components and the disposal of soiled mixtures. The total costs of this aqueous process should also be considered.

### b) Formulated hydrocarbons: Bi-co-solvent vapor process 2

Formulated hydrocarbons have been developed mainly after the CFCs and HCFCs ban and when perfectly formulated, easily outperform any other cleaner. They are able to remove flux residues, solid residues and salts under any type of components because of their very low surface tension (approx. 20mN/m). With the Bi-co-solvent vapor process 2, the PWAs are very thoroughly rinsed and dried in the vapor phase. Fluorinated solvents are used in the vapor phase system, having the lowest surface tension of all families, approx. 8-15 mN/m. The rinsing solvent can be recycled by distillation and the formulated hydrocarbon is removed easily. The lifetime of the formulated hydrocarbons is very extensive and the total costs are the lowest of all types of cleaning processes. The surface tension of the vapor process 2 is outstanding to reach specifications. Please see figure 2. When combined with formulated hydrocarbons, the co-solvent process is excellent to go through the toughest specifications. It is one of the most user-, safe- and environmental-friendly process.
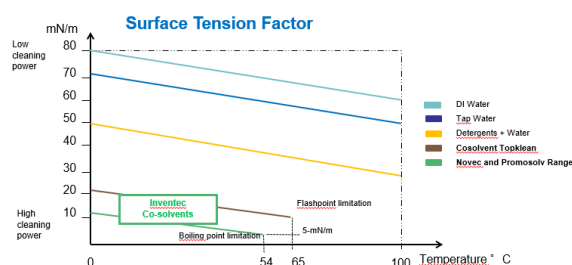


## Table 2: Product families and formulations (in blue and green, products selected for the study)

| | Product Family | Formulations |
|---|---|---|
| 1 | Detergents | Surfactants, wetting agents, salts and water |
| | Petroleum distillates light | Alcohols, ketones, AII Class |
| 2 | Formulated Hydrocarbons | Aliphatic, cyclo-, iso- paraffins, with additives, AIII class |
| | Brominated solvents | n-Bromopropane blended with alcohols |
| | Glycols or modified alcohols | Mono-propylene glycol, others, additives and water |
| 2 | Fluorinated solvents | Nonafluorobutyl-methyl ether, others |

## 5) Trial analysis flow

Four PWAs were processed and separated into 2 groups: in-line aqueous wash process 1 and Co-solvent vapor cleaning process 2. They were observed before and after each process cleaning (OP). Then, they ran through the C3 Surface ionic extractions (CI) and the solution analysis (CM). The extracted solutions from C3 were then used for the Ions chromatography (IC). Please see Figure 3.

## Figure 3: Trial analysis flow chart
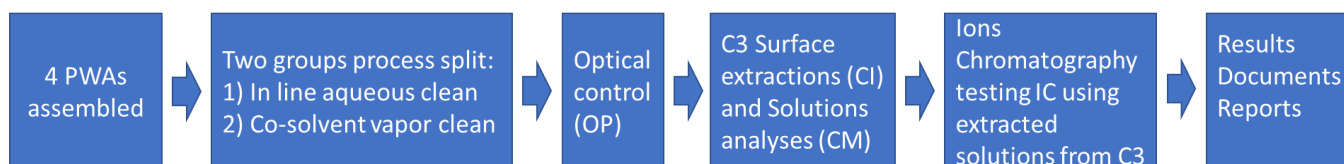
## 6) Optical control: OP

The optical control was made with a binocular microscope. Please find here some pictures. **Picture 2, not cleaned board.** Some residual flux can be seen on every pad after the assembling. The purpose is to visually compare the co-solvent vapor cleaning process versus the aqueous cleaning process. It appears that residues are mostly gone with the aqueous process, whereas it is completely removed with the vapor degreasing process.
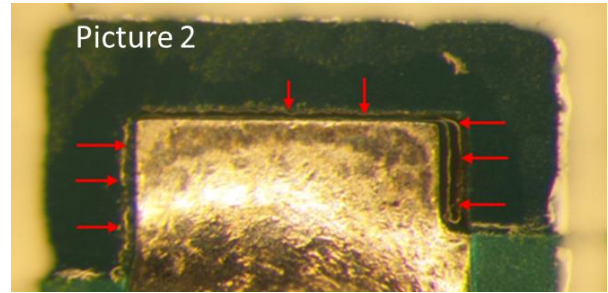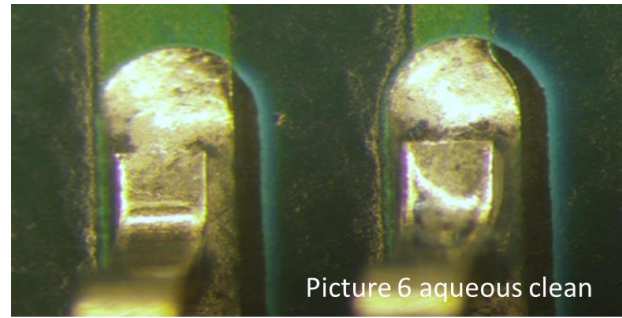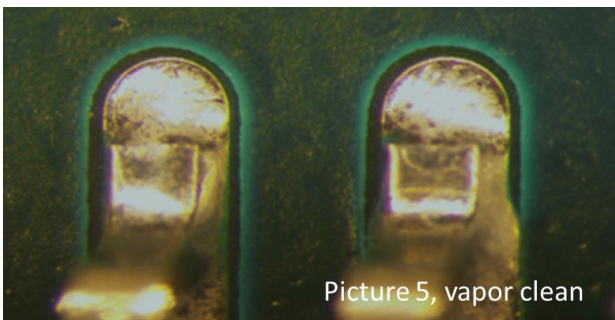

Picture 2

**Picture 3, Vapor cleaned.** Flux is removed          **versus**          **Picture 4, Aqueous cleaned, some flux residues**
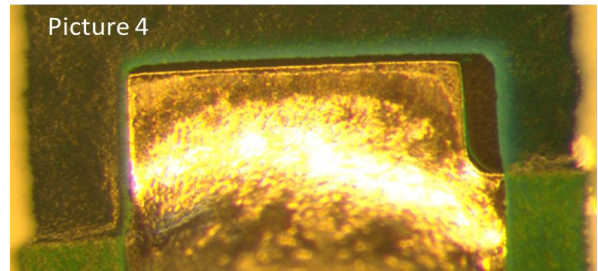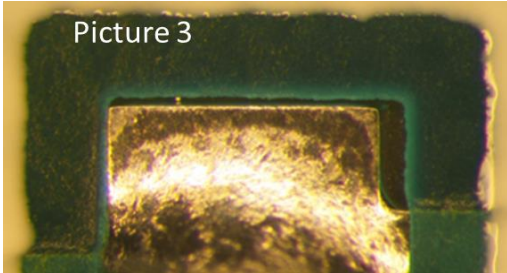

Picture 3


Picture 4

**Picture 5, vapor cleaned**          **versus**          **Picture 6, aqueous cleaned:**


Picture 5, vapor clean


Picture 6 aqueous clean

## 7) C3 Surface extractions (CI) and Conductivity reading (CM)

Components A, B, C on picture 1 were targeted as C3 surface ions extraction and solutions analysis. PWAs cleaned with the aqueous cleaning process, were boards 1 & 2 and with co-solvent vapor cleaning process, were boards 3 & 4. Sampling were made at position: A= U9, 20P QFN / B= U18 8P SOIC / C= U10 8P SOIC. The C3 surface extraction is done with equipment using water steam vapor at 124°C on the specific surfaces selected here A, B, C. These specific surfaces are encapsulated with special syringes, which will collect the extracted ions with the water steam. The extracted solutions are plotted for 120 Sec. and when the current measured is


Picture 1

less than 250mA, then the sample is estimated "Clean". When the current is above 250mA before 120 Sec, the sample is considered as "Dirty". Please find here some typical recordings:
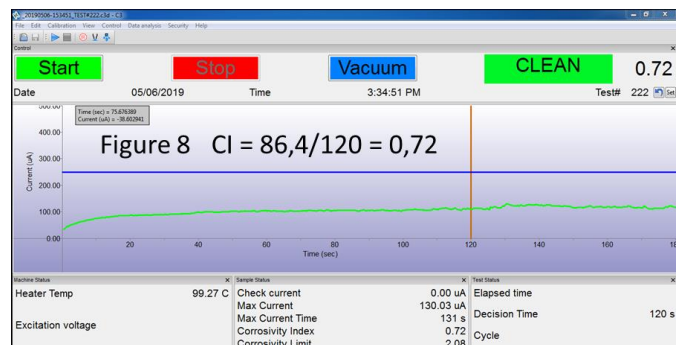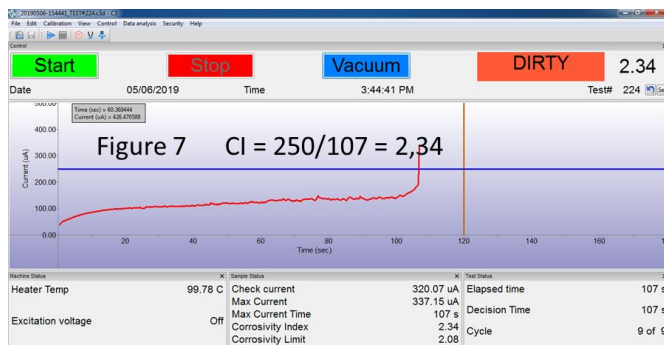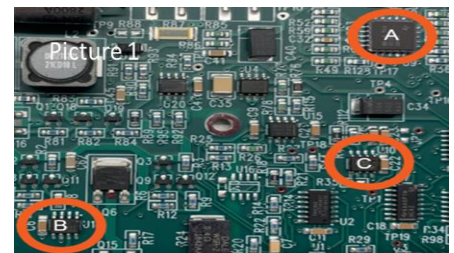




**Figure 7: "Dirty"    and    Figure 8: "Clean"**

<u>**CI = x mA/120Sec**</u>          **If CI is of > 2.08 = "Dirty"**          **If CI is of < 2.08 = "Clean"**

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The conductivity was also measured with a conductometer when the samples were at room temperature 25°C.

**Table 3: Corrosivity Index (CI) and Conductivity Meter Readings (CM)**

| Cleaning Process | | Chips | C3 max I | Time | CI | Results | CM (μS/Temp) (25°C) |
|---|---|---|---|---|---|---|---|
| Aqueous | 1 | A | 128,32 | 178 | 0,72 | Clean | 4,5 |
| | 1 | B | 132,59 | 178 | 0,75 | Clean | 2,5 |
| | 1 | C | 141,74 | 173 | 0,82 | Clean | 2,6 |
| Co-solvent vapor | 2 | A | 72,50 | 123 | 0,59 | Clean | 2,7 |
| | 2 | B | 131,37 | 177 | 0,74 | Clean | 2,5 |
| | 2 | C | 56,5 | 101 | 0,56 | Clean | 2,8 |
| Blank test cell glass 3 | | X | 139,79 | 173 | 0,81 | Clean | 3,1 |

## 8) Ion Chromatography: IC

These samples were gathered into a new neutral samplers' kit and were then sent to an external lab equipped with an ion chromatograph. No detail about the trials was given except the samplers' kit with the referenced numbers as shown below: **Please see Figure 9 below.** The ions measurements were plotted in **Table 4**.

Position 1A, 1B, 1C, aqueous cleaning process 1 and chips

Position 2A, 2B, 2C, Bi-co-solvent vapor cleaning process 2 and chips

Position 3X, Blank test cell glass, no chip.

Last position is empty.

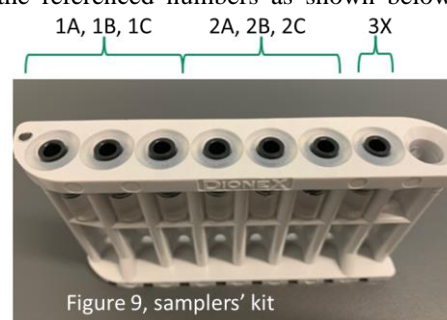In this study, no base line evaluation of a not clean sample was performed



Figure 9, samplers' kit

## Table 4: Ion Chromatography Measurements

| Anions IC | Fluoride | Chloride | Bromide | Nitrite | Nitrate | Sulfate | Phospate | Total inorganic anions |
|---|---|---|---|---|---|---|---|---|
| Tesla limits for washed PWAs (μg/in.sq) | < 1 | < 2 | < 10 | < 4 | < 4 | < 4 | < 4 | NA[1] |
| 1A- Aqueous | - | 1,80 | - | 9,83 | - | 0,10 | - | 11,73 |
| 1B- Aqueous | - | 1,22 | - | 9,87 | - | 0,19 | - | 11,28 |
| 1C- Aqueous | - | 1,20 | - | 9,73 | - | 0,10 | - | 11,03 |
| 2A- Vapor | - | 1,51 | 0,79 | - | - | 0,93 | - | 3,23 |
| 2B- Vapor | 0,35 | 1,10 | 0,83 | - | - | - | - | 2,28 |
| 2C- Vapor | - | 1,66 | 0,97 | - | - | - | - | 2,63 |
| 3X- Blank/Control | - | 2,044 | - | 9,801 | - | 0,18 | - | 12,03 |

**NA[1]:** No industry recommended values have yet been established

## 9) Results and Observations

These trials have clearly demonstrated that the cleaning performances can be further improved with a segregated Bi-co-solvent vapor cleaning process versus an aqueous one. These trials were made for 10 Minutes in the co-solvent to be comparable to the aqueous process, whereas the standard cleaning cycle recommended is between 3 to 5 Minutes. The cleaning cycle time being on purpose comparable, actually, the solvency power and the surface tension allow to clean underneath the low standoff pack-

ages. Table 3 shows that the Corrosive Index CI is lower for the vapor process because of lower maximum current intensity and a shorter running time. The average of the different values is 0.76 for the detergent versus 0.63 for the co-solvent process.

The conductivity meter measurements CM are showing only a little advantage for process 2, but probably because of the system measurement limitations and the ions in presence. With these data, it seems that the two different processes give acceptable results.

Then it drives us to consider the results measured by the ion Chromatography. This ion chromatography provides extended measurements to a conventional ionic contaminometer, which creates the issue of calculating some ionic residues all over a surface, expressed in µg of Eq NaCl/cm2. Effectively, the ionic surface extraction on and under components with water vapor steam, followed by the Ion Chromatography, demonstrates the contaminometer limitations and provides extended values in Table 4. Results shows that the cleaning performance are between 3 to 5 times improved for the segregated co-solvent vapor cleaning process versus the aqueous. The miniaturization is source of issues precisely for Class 2 and Class 3 PWAs products. (Automotive, military, medical and space products). This table 4 shows that the sums of the ions of interest is 3 to 5 times higher for the detergent process compared to the co-solvent one. The main difference comes from the presence of nitrite ions for the detergent, which are not observed for parts cleaned with co-solvent. The nitrite may come from the contamination of the parts during the previous steps of manufacturing or the detergent itself, not being rinsed efficiently under the low standoff with DI water (having a surface tension of around 73 Dynes/cm at 20°C). This amount of nitrite for the aqueous spray in-line process is above the specifications for Class 2 and Class 3 PWAs products.

For the other ions detected, the chloride ions are found equivalent for both processes. It seems that the source of these ions is not totally cleaned, but nevertheless in the specifications. Some pollutants are found only for the solvent process like fluorinated or brominated in small quantities below specs.

Solvents not being chlorinated nor brominated, the question is where these ions are coming from? Actually, we can suspect, when the epoxy resin in the laminate is cured, small quantities of sodium chloride is formed as a by-product. To render some resistance against fire, brominated flame retardants are added to the laminate. Also, some decomposition may occur during soldering processes: hydrogen bromide is liberated. Chloride and bromide ions quantities are then extracted by the C3 and measured by the IC and remain small, thus it is difficult to conclude. It could be a flame-retardant contamination which is revealed by the use of fluorinated solvent (halogen family) and then, only partially removed?


## 10) Conclusions and observations

This cleaning study shows, how the miniaturization and low stand-off cleanliness is achieved with the bi-co-solvent vapor cleaning process versus a standard aqueous cleaning process.

Actually, the cleanliness performed is 3 to 5 times improved with the segregated co-solvent process versus the aqueous one. It was demonstrated visually and by ion chromatography.

The ion chromatography (IC) combined with a local ion surface extraction C3 (CI) on chips, have demonstrated that whereas a contaminometer calculates an average of contamination spread on a PWA surface, this IC method, based on IPC Norm, TM-2.3.28b, brings further detailed results in favor of the co-solvent process.

Thus meaning, the surface tension is a key factor to remove contaminants and clean the residues under the low stand-off components to guarantee high reliability, performance, long lifetime and the best coated surface quality.

This cleaning trial with the segregated Bi co-solvent vapor cleaning process, could be further improved with mechanical cleaning actions to remove contaminants under the low stand-off components to guarantee higher reliability, performance, long life and a better coated surface. Here, for the purpose of this test, a basic agitation was used.

The Cell Glass Blank/Control slide was obviously not the cleanest reference sample null as it should be.

Further testing could be pursued for SIR control.


## 11) Bibliography

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