Cleaning PCBs in Electronics: Understanding today’s Needs  

P.J.Duchi, Anne-Marie Laügt, Marie Verdier, G.Abidh  
Inventec Performance Chemicals  
Bry sur Marne, France  

Abstract  
Because of the phase out of CFC’s and HCFC’s, standard solder pastes and fluxes evolved from RA and RMA fluxes, to No-Clean, to low residue No-Clean, to very low residue No-Clean. Many companies came out with their cleaning solutions, aqueous and semi-aqueous, with each product release being more innovative than the previous one. Unfortunately for most of the suppliers of cleaners, two other trends appeared; lead-free soldering and the progressive 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. Also, assembly processes have been modified due to smaller components and more compact board assemblies. Thus, it is important to remember that the world is composed of two main things: organics and inorganics. Organics are made of resins and activators, whereas inorganics are made of salts, metallic salts and fillers.  
Cleaning performance is affected by three main criteria. The first involves the Hansen Parameters which is a characterization of a contaminant to be dissolved and which can be simplified by the solvency power of a product also known as the Kauri Butanol Index (KB Index). The second is surface tension, expressed in mN/m. This parameter must be considered because when the cleaning product cannot make contact with the contaminants under or around components, the contaminants cannot be dissolved. This second parameter drives us to the third point, which is physical parameters like temperature, mechanical activities, and the duration of the process.  
The mastery to manage all of these parameters while facing high-tech miniaturization and environmental care, like ROHS, REACH, etc. brings innovation to cleaning in this electronic world.  

Introduction  
Cleaning PCBs has been a vast topic for many years, particularly so since the ban of CFCs and HCFCs. These products offered solvency power, low surface tension properties to dissolve, remove and dry within minutes any parts of any design. The electronic industry has grown so rapidly since the 80s, that today, nearly 50% of any individual’s belongings are composed of electronics: e.g.: Mobile phones, remote controls, TVs, radios, cars, iPods, computers, HiFi, hard discs, memory sticks, cameras, videos, refrigerators, dish and laundry washers, cars, planes, satellites, implants, etc…  
Since the 90s, the electronic evolution has been exponential, and the miniaturization has advanced proportionally. The introduction of such new small parts not only raised some design problems, but also some practical aspects such as handling and some reliability problems. In meantime, the suppliers of solder fluxes and pastes had to adjust new formulations for the new markets, the new demands and the new regulations.  
Accordingly, the electronic suppliers adapted their production to the customers’ demands with cleanable and no clean fluxes, also called consumable devices. The non consumable devices such as medical implants, military tools, satellites, safety parts for cars, trains, medical equipments and many other products, should be reliable and thus cleaned. To achieve a good cleaning result, it is worth understanding the various parameters present and the physical laws which are ruling this chemical operation.  
Cleaning has a cost and it should be adapted to the needs while maintaining stability in time, efficiency, quality and performance.  

1) Miniaturization  
Today, miniaturization is a hundred times greater than during the 80’s. This reduction in size means reduction of solder pads and also amount of flux residues. But it also means a reduction of space between legs and board/components. Today, size of components are down to 0,1mm. In addition, the components became of high capacity with resistors, diodes, quartz, selfs, BGA and others. The reliability of these components should be always increased. This miniaturization should not become a reason of instability and unreliability. The cleanliness should be performed and pass the norms. (Figure 1)
2) Contaminants

The contaminants on a circuit board are mainly composed of: organics such as natural and/or synthetic rosins, ions, acids, solder balls, finger prints, and particulates of PCBs. The lead-free alloys need higher soldering temperatures than the standard Sn/Pb which are carrying significant evolutions on the fluxes to be used. These fluxes are most of the time more active and must resist to higher reflow profiles. They present more risks than the one formerly used, and the temptation is high to choose production parameters allowing shining soldering pads. The ionic cleaning of the PCBs is then more critical before tropicalisation, but will also help to control the assembling process and help to establish final assembly lifetime. The ionic contamination is a good quality indicator for the long term reliability. Please see Figure 2.

3) Specifications set up

Every end-user has his own typical specifications which are depending on his own or his customers. For this study, the specifications have been taken as described in Table 1. Six hundred PCBs for trials were produced in large quantities to triple the cleaning results (Figure 3). Each trial contains 30 components. All residues must disappear, including the contaminants under the components. No fingerprint, particle nor dust should remain, including residues of cleaning products. The components, the rosins, the underfill and the substrate should not be damaged by the cleaning operation. The parts should be dried at the end of the washing step. The ink markings should be resistant to the cleaning.
4) Cleaning products available

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).

a) The detergents

Detergents A are good most of the time, but very specific to the type of fluxes 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 20-60°C, and the agitation used, sprays, spray under immersion or ultrasonic’s should be considered. It is the aqueous cleaning process. The drawbacks of these detergents are: the removal of all residues under components because of the poor/high surface tension included between 40-50mN/m, the aggression 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 and the disposal of soiled mixture. (Figure 5). The total cost of these should also be considered.

b) The petroleum distillates

The petroleum distillates B, such as alcohols and ketones are mainly used for the cold cleaning operation, even though used they can be found used at warm temperatures. There should be no need to mention that these products are very flammable at room temperatures and used under warm conditions are very risky. Costs are acceptable, but disposal and annual cost can be significant.

c) Formulated hydrocarbons

Formulated hydrocarbons C have been developed mainly after the CFCs and HCFCs story 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). They must be rinsed with a rinsing product which can be water or solvent (fluorinated base F). The water rinse system is the semi-aqueous process and the solvent based system is a co-solvent process. With the aqueous process, the same detergents’ drawbacks are found, where as, with the co-solvent process, the PCBs are very nicely rinsed and dried with the vapour phase. The rinsing solvent can be recycled by distillation and the formulated hydrocarbon is disposed easily. The lifetime of the formulated hydrocarbons is very extensive and the total costs are the lowest of all type of cleaning systems. The surface tension of both C and F are outstanding to reach specifications. It is one of the most user- and environmental- friendly process.
d) Brominated solvents

The brominated solvents’ formulations are very simple to use into a vapour phase degreaser. Nevertheless, some non-solvency problems and compatibility problems can be found. For this reason, compatibility tests must be done with all materials in contact. Even though with the very low surface tension (20-30mN/m), the ions might not be totally removed and prevent matching ionic specifications. The costs are reasonably low, but the hazardous aspects for end-users and the environment are of great concern. These products are severely restricted in Europe. (Figure 4)

e) Glycols or modified alcohols

Glycols or modified alcohols formulations are used the same way as the formulated hydrocarbons with some surface tension between 25 and 35 mN/m. Unless using a formulation, they can not solubilise all contaminants. In most of the cases, they have a good solvency power, but the disadvantages of these products are the rinsing with tap or DI water (high surface tension: approx, the drying operation, the water-proof compatibility and the disposal of soiled mixture (Figure 4). The total cost of these should also be considered as high.

f) Fluorinated solvents

When used pure, fluorinated solvents and formulations can not solubilise all contaminants. Even with the lowest surface tension of all families, approx. 8-15 mN/m, their solvency power is weak. (Figure 4). But when combined with formulated hydrocarbons, then the co-solvent process is excellent to reach the toughest specifications. These products should be used in the latest solvent vapour degreasers.

<table>
<thead>
<tr>
<th>Product Family</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Detergents</td>
<td>Surfactants, wetting agents, salts and water</td>
</tr>
<tr>
<td>B Petroleum distillates light</td>
<td>Alcohols, ketons, AII Class</td>
</tr>
<tr>
<td>C Formulated Hydrocarbons</td>
<td>Aliphatic, cyclo-, iso- paraffins, terpenes with additives, AIII class</td>
</tr>
<tr>
<td>D Brominated solvents</td>
<td>n-Bromopropane blended with alcohols</td>
</tr>
<tr>
<td>E Glycols or modified alcohols</td>
<td>Mono-propyl glycol, others, additives and water</td>
</tr>
<tr>
<td>F Fluorinated solvents</td>
<td>Nonafluorobutyl-methyl ether, others</td>
</tr>
</tbody>
</table>

5) Solvency Power

The solvency power is the simplest way to express the strength to dissolve the contaminants. Nevertheless, the full method is the Hansen parameters which will define for any product, some parameters of polar, non-polar and hydrogen bonding. It will establish a tri-dimensional chart of solvency power. It is true for theoretical calculations, but when products are blended, then the Kauri-Butanol method allows to establish a direct rosin solvency value which can be shown on Figure 4. This chart is fairly representative of the different product families seen in paragraph 4.

Figure 4: Kauri-Butanol index chart
6) The surface tension factor
The surface tension factor is a key issue to understand a good cleaning performance. It is so important that the miniaturization is another running parameter. The smaller the PCBs become, the lower the surface tension of the cleaners should be. When this law is understood, half of the cleaning is achieved.

Let’s consider demineralised water (A) which has a surface tension of around 80mN/m (Figure 5). This line is bending as a function of the increase of the temperature. The variation is of about -10 mN/m. It is the reason why cleaners are warmed up into washing units; to reduce the surface tension and to move underneath cavities and components. There is the same issue with tap water (B), where its surface tension starts at 70mN/m at room temperature.

When Detergents (C) are added to water, the surface tension of the medium drops down to 45-35 mN/m, according to the temperature of use. However, the big question remains, how can a “wetting product” can be rinsed with some water which has a higher surface tension? For this reason many suppliers are using additives or simple isopropanol, to better rinse, wet and dry parts.

To get underneath the components, Glycols (D) or formulated hydrocarbons (E) are commonly used. Their surface tensions are lower than water and detergents, between 25-35 mN/m for the first and around 20mN/m for the second. The same rinsing problem remains for these products with water, rather, use a selected final rinsing solvent which has a lower surface tension than these cleaners and which will finally dry the PCBs.

As solvents evaporate and condense on the free-boards of the vapour phase equipment, no residues are left on the PCBs and the surfaces, including under the components. (Figure 5)

Figure 5, Surface tension chart

7) Mechanical agitations
There are many sort of mechanical agitations; sprays, sprays under immersion, ultrasonics, agitations, rotations etc. These agitations provide an additional cleaning parameter which helps to penetrate, to dissolve and to unfasten contaminants. This study evaluates all type of mechanical agitations and compares their efficiency. Many times, industrial PCBs assemblers, avoid ultrasonics because of some fears about the components and, specifically, with quartz. The trials, which have been run over 60 different quartz, accordingly to Norm IPC-TM-650 demonstrate that none of them have been affected nor damaged (Figure 7). The benefits of the ultrasonics are easily demonstrated. (Figure 6)

Figure 6: Quartz cleaned with ultrasonics. No damage
8) Cleaning results
Table 3 is expressed as a ranking comparison of the various cleaning trials. Every cleaning comparison per type of flux residues was tripled. All PCBs have been observed and pictures have been made. The comparative results have been made as a function of the specifications established previously. Ionic contamination for the best cleaning process remains below 0.2 μg of Eq NaCl/cm².

Table 3. Comparative Results of cleaning

<table>
<thead>
<tr>
<th>Cleaning process</th>
<th>Product Family</th>
<th>Equipment type</th>
<th>Comparative Scale (1:10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspersion, aqueous</td>
<td>Detergent 1</td>
<td>Dish washer type</td>
<td>4</td>
</tr>
<tr>
<td>Immersion US 40 kHz, aqueous</td>
<td>Detergent 2</td>
<td>Sumps in line</td>
<td>1</td>
</tr>
<tr>
<td>Immersion jets, semi-aqueous</td>
<td>Glycol formulation 3</td>
<td>Sumps in line</td>
<td>3</td>
</tr>
<tr>
<td>Immersion US 40 kHz, semi-aqueous</td>
<td>Glycol formulation 3</td>
<td>Sumps in line</td>
<td>7</td>
</tr>
<tr>
<td>Immersion US 30 kHz, mono-product</td>
<td>Glycol formulation 4</td>
<td>Vacuum machine</td>
<td>7</td>
</tr>
<tr>
<td>Immersion US 40 kHz, semi-aqueous</td>
<td>Glycol formulation 5</td>
<td>Sumps in line</td>
<td>1</td>
</tr>
<tr>
<td>Immersion, co-solvent mixed</td>
<td>Form hydrocar/HFE</td>
<td>Vapor degreaser</td>
<td>4</td>
</tr>
<tr>
<td>Immersion, co-solvent mixed</td>
<td>Form. hydrocar70/HFE</td>
<td>Vapor degreaser</td>
<td>2</td>
</tr>
<tr>
<td>Immersion US 25 kHz, co-solvent sep</td>
<td>Form hydrocar/HFE</td>
<td>Co-solvent/vapour degreaser</td>
<td>9</td>
</tr>
<tr>
<td>Immersion US 38 kHz, co-solvent sep</td>
<td>Form hydrocar/HFE</td>
<td>Co-solvent/ vapour degreaser</td>
<td>9</td>
</tr>
<tr>
<td>Immersion Jets, co-solvent separated</td>
<td>Form hydrocar/HFE</td>
<td>Co-solvent/vapour degreaser</td>
<td>8</td>
</tr>
<tr>
<td>Immersion US 40 kHz, vapour phase</td>
<td>Brominated solvent</td>
<td>Vapour phase</td>
<td>4</td>
</tr>
</tbody>
</table>

9) Conclusions
This cleaning study shows that there are many cleaning parameters affecting its efficiency. The final aspects and performances of these PCBs are based on the mastering of cleaners, size of the assemblies, agitations and the cleaning processes. When the choice is based on solvency power, the lowest surface tension and the most efficient process, rather than ideas and opinions, then a perfect job can be reached matching the toughest specifications. The co-solvent / Vapour degreaser process with formulated hydrocarbon and HFE (hydrofluoroether), combined with ultrasonics or jets show the best performance. Contamination is below 0.2 μg of Eq NaCl/cm² for ranking 9 and with a perfect visual aspect under components. No damage of quartz could be notified during trials.

10) Bibliography
Inventec Performance chemical SA, processing guide, France & Switzerland / IPC Norms / Valtronic technologies Switzerland.