Use of High Purity Water to Eliminate Contamination
And Achieve Cleanliness- A Discussion of Performance and Costs

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Abstract

PCB board manufacturers engage in a number of wet processes. Water is used ubiquitously in many of these processes for rinsing as well as bath make-up. The impacts of water quality on production processes and product quality are many times ignored. Cleaning surfaces to achieve defined levels of cleanliness in terms of particle and other contamination is now a topic of new ISO standards. Many PCB sites do not use high quality water due to the assumption of high costs. This paper discusses how high purity DI water can be produced at lower costs using a DI recycling approach using a technology called EDI (electrodeionization – which is an electro-membrane technology), in PCB production. A discussion of this new technology that allows lower costs of DI production and recycling will be presented. This paper will also present customer and various third party data on how high purity water reduces contamination build up on parts, during processing, improving product quality and reducing rejects.

Introduction

Continued miniaturization of high technology products in a wide range of industries has resulted in the increased need for cleaner parts. Contamination on the surfaces of electronic parts and mechanical assemblies can degrade performance, production yield and life expectancy of a product. Manufacturers have instituted cleaning procedures to ensure their precision component parts are clean and unlikely to adversely affect the completed product.

Also, as use of solvents in cleaning applications has been phased out with water, many users have moved to water-based cleaning and rinsing. Various wet processes use water to remove contaminants or chemistry after processing, such as coating and plating from the various chemistries used for PCB processing. Good water quality is fundamental to any aqueous process system. Excessive water hardness and total dissolved solids (TDS) limit the effectiveness of process effectiveness leading to surface contamination and built up impurities and residues on interconnection.

Softened water is not the answer. The softening process simply replaces heavier elements in the water with sodium. Sodium and other dissolved solids such as chlorides; sulfates and calcium salts remaining on the metal surface can initiate the corrosion process, causing delamination, even if the final rinse contains an acidified sealer.

Water is increasingly the most important raw material in the printed circuit board industry, in terms of quality and quantity, used in electroplating and other coating/finishing processes. However, most users in the PCB industry spent the least amount of resources on assuring high quality water for their processes. An average plating bath is made up of 80% water.

Most steps in plating and wet process operations are followed by one or more water rinses. Water can also be the cause of many problems in these operations. The source of raw water used in PCB shops for bath make-up and rinsing can be:

- City water from a municipal water supply,
- Raw surface water from a river, lake or reservoir,
- Raw ground water from a well or spring, or
- Overflow cooling water.

Water coming into a PCB shop contains impurities which may impair the processes and impact product quality. Table 1 below lists components of water and the problems encountered by their presence.
Table 1 - Impurities Present in Water Which may be Harmful to Plating and Coating Processes

<table>
<thead>
<tr>
<th>Impurity Type</th>
<th>Problems Caused by Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved mineral salts (ions)</td>
<td>Relatively insoluble in water, solubility decreases on heating, and may concentrate with evaporation creating a film or scale on work pieces and sludge in the water</td>
</tr>
<tr>
<td>calcium and magnesium (hardness)</td>
<td>Substantial amounts may cause brittleness of nickel plate or lower the maximum allowable current density</td>
</tr>
<tr>
<td>sodium and potassium</td>
<td>May cause various problems such as diminishing the activity of ingredients in plating and coating baths; gives water a characteristic color</td>
</tr>
<tr>
<td>heavy metals (present as salts)</td>
<td>Requires the use of corrosion-resistant lines and tanks, requires added alkali for neutralization</td>
</tr>
<tr>
<td>acids (present as salts)</td>
<td>When heated, converts to carbonate which forms precipitates with calcium</td>
</tr>
<tr>
<td>Dissolved organic salts such as bicarbonate</td>
<td>Carbon dioxide is corrosive in itself; in solution it forms carbonic acid which lowers the pH and accelerates corrosion; dissolved oxygen is highly corrosive to iron and steel</td>
</tr>
<tr>
<td>Dissolved gases such as carbon dioxide, oxygen, and nitrogen</td>
<td>Objectionable for most uses</td>
</tr>
<tr>
<td>Un-dissolved matter such as turbidity (suspended matter) and sediment (suspended matter which settles rapidly)</td>
<td>May cause staining, slimy deposits or clogging of pipes</td>
</tr>
<tr>
<td>Microorganisms</td>
<td></td>
</tr>
</tbody>
</table>

Rinse and Make up Water Quality - Why is Water Quality Important?

The concentration of these impurities is measured in terms of parts per million (ppm). One ppm is equal to 0.001 gram (1 milligram) dissolved in a liter of water. Minute amounts of a single impurity can create major problems and result in lost time, materials, profits and possibly, customers. In the case of decorative plating, water spots and stains caused by impurities are objectionable and may require reworking, wiping or buffing. This adds to the cost of operation and, in the case of buffing, may reduce the corrosion resistance of the finish. The presence of 10 ppm of chromates in a nickel bath has the effect of decreasing the upper current density limit resulting in an unsatisfactory deposit.

Impurities in incoming water may be present in such low concentrations that they do not cause problems, but may become concentrated in heated plating baths or due to evaporation. Concentration of impurities can readily reach levels high enough to cause failure of the bath chemistry. An example of this is chlorides in an electroless nickel bath. Another important consideration is the effect of water quality on recovery of metals from process solutions. Impurities in the water may cause a recovery technique to fail or operate inefficiently. An effective use of ion exchange is the removal of hard water and other mineral salts prior to plating to render metals recovery more cost effective. The ion exchange resin for hard water ions is less costly than resin for heavy metals.
Techniques to Improve the Quality of Incoming Water

Many PCB shops employ some form of water pre-treatment. Municipal water supplies are generally clear and low in color, low in iron and manganese, safe for drinking purposes, but not sufficiently soft or low in total solids for all plating uses.

With current technology, it is possible to treat any raw water to be acceptable for plating and metal finishing. The costs associated with poor quality work outweigh the costs of water purification. Treatment of raw water to remove these impurities is accomplished mainly by ion exchange and reverse osmosis which are also used for wastewater treatment or metals recovery.

Ion Exchange
Ion exchange is used in about 95% of all water purification applications. Ion exchange purifies water by:

- Softening which uses a cation column to remove hardness (iron, calcium and magnesium), or
- Deionization (or demineralization), which uses both cation and anion columns to remove essentially all ionized substances (mineral salts) dissolved in water.

Reverse Osmosis
Reverse osmosis (RO) is a crossflow membrane filtration system used to purify raw water for use as rinsewater. RO produces water similar in quality to demineralized or distilled water by removing organic contaminants and inorganic salts.

Advanced Electrodeionization (AEDI) for Process Rinse Water Recycling
The company has developed a product to recover and make high purity DI water in point of use, for wet process applications. This concept is to replace the conventional D.I./ion exchange pretreatment system with an Advanced Electrodeionization (AEDI) system and continually to recover and reuse the DI water that is much needed for most processes, but commonly is believed to be too expensive to produce.

Advanced Electrodeionization (AEDI) removes Ionizable constituents from water using ion exchange membranes, ion exchange resins, and a DC electrical potential. AEDI provides two technologies in one module: electro dialysis and ion exchange. Ion exchange membranes separate an ion exchange mixed bed from electrodes. The ion exchange resins remove ionic matter from process water and the electrodes provide electro-regeneration of the resin when energized by a DC rectifier. AEDI systems provide a superior separation of ionic process solutions from wastewater and process water. AEDI applications include direct recovery of electrolytes from active rinses as well as recovery and recycling of process water and wastewater in industrial applications. Figure 1 shows a typical interior of a stack.

The AEDI requires water of certain quality or spec so it can operate most efficiently. This is why, the initial start-up of the system has to be with DI water quality. No hardness should be present or silica in the water when the system is started up. The system can then maintain the high grade of water and remove effectively all process impurities. The company also now offers besides the standard modules a high temperature module for medical applications.

The usual feed water source maybe RO water or process direct feed water if it has been previously DI or RO. The system can accept low pH to slightly higher pH and online pH adjustment is also available. The system must be receiving feed water with zero or no particulates or silica.
AEDI systems can remove the impurities that can cause damage to parts during processing/production. For example, AEDI removes ion loads, and oxidizers from the incoming water used for rinsing. The continuous removal of impurities allows the process rinses to run contaminant free.

Table 2 shows a list of select industries and their application needs for particulate cleanliness, as well as the typical particle size of concern for the impurities that are allowed on the parts.

The complexity of rinse cleaning systems leads to a variety of potential problems including:

- Filter loading and failure
- Water supply issues
- Unusually dirty incoming parts or parts of different contamination levels

Deionized water can help manufacturers achieve particulate free processing and run processes contaminant free – and online water recovery and re-purification allows for unlimited high quality water for reuse.

Why a point of use recycling system?
A typical ultrapure water production system includes reverse osmosis, ion exchange, instruments and controls, degasification equipment, filtration equipment, pumps and valves, storage and piping, and disinfection – a lot of efforts and activities. It is vital that every component of the ultrapure water (UPW) system consistently maintain high purity. All in all, plenty of resources and costs are associated with the operation of such systems.

Ultrapure water specifications maybe varied by site or the type of manufacturing operations. For example, in semiconductor or disk drive processing, incoming rinse water has to meet Total Organic Compound (TOC) limit of 0.05 ppb as well as a consistent resistivity of 18 Megohm.cm. At 25°C, 18 Megohm.cm is the maximum resistivity that is practically achievable and measurable under industrial conditions. At such high resistivity (low conductivity) the accuracy of process instrumentation becomes critical and specialized materials are required where process equipment comes into contact with water to ensure no contaminants are released into the product water.
<table>
<thead>
<tr>
<th>INDUSTRY</th>
<th>APPLICATION</th>
<th>PARTICLE SIZE OF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro Electronics</td>
<td>Tool Components</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td></td>
<td>Wafer Handling and Storage</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td></td>
<td>MEMS Sensors</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td>Data Storage</td>
<td>Tool Components Drive Components</td>
<td>100 nm - 500 nm</td>
</tr>
<tr>
<td>Aerospace</td>
<td>Sensors</td>
<td>&gt;2 microns</td>
</tr>
<tr>
<td></td>
<td>Fuel Components Specialty Parts</td>
<td>&gt;2 microns</td>
</tr>
<tr>
<td>Automotive</td>
<td>Sensors</td>
<td>&gt;2 microns</td>
</tr>
<tr>
<td></td>
<td>Fuel Injectors</td>
<td>&gt;2 microns</td>
</tr>
<tr>
<td>Medical Devices</td>
<td>Implants</td>
<td>&gt;10 microns</td>
</tr>
<tr>
<td></td>
<td>Production Equipment</td>
<td>&gt;10 microns</td>
</tr>
</tbody>
</table>

It has been believed for many decades that fresh water must be used to make UPW for any wet process or tech. manufacturing operations. This paper discusses, how water already purified for production uses, (process water) can be recycled at “point of use” (POU) and returned back for reuse in to the same process; or to secondary polish before reuse.

Today many customers are facing the high costs of water resources purification and management, and so today more than ever the concept of POU recovery and reuse of UPW makes sense.

The AEDI product allows recovery and reuse of water at POU – either at the tool or a bay of tools, with a fully integrated system. This approach allows for re-purification and re-make of DI water to original specs by continuously removing impurities from the process.

In wet process application, the variety of chemistries (such as etch, cleaning, etc.) is normally followed by rinsing processes. Mixing of the various wastewater streams coming from each chemistry may not be compatible, and can cause issues for wastewater treatment as well as for effective water recovery systems that handle the mixed wastewaters. In cases, where the chemistries are compatible, as much as 90% of the rinses can be recovered for reuse. The recovered rinses may be sent back to the tool directly or re-polished to assure purity levels are consistent with the facility’s in-house specs.

In the coming years, as chemistries evolve, and more complex processes are instituted, water recycling of mixed rinses results in lower recovery rates; and thus are less efficient. For example, new plating chemistries are being introduced to semiconductor processes. These chemistries require additional treatment if drained to central waste treatment systems – and the conventional acid waste neutralization processes will no longer suffice. So additional waste treatment has to be added which increase the cost of waste treatment. For example, facilities have to install precipitation, reduction/oxidation, or other treatments to deal with these complex chemistries.

POU allows for the removal and separation of these specific chemistries and allows for off-line recovery and recycling of these materials in particular if they have value. These chemistries, not only are expensive in many instances, but if they are metal-based (such as copper, cobalt, etc.) they will be more recovery worthy.

The point of use recovery results in avoidance of the disposal after one use, thus the continuous need to fresh water and waste treatment, on site or offsite. POU recycling and reuse allows manufacturing customers to reduce cost of production substantially. It eliminates the continuous consumption cycle and replaces it with complete re-utilization of material and resources.
Case Study: POU Rinse Water recycling

PCB Line Case Study

The Company has gathered cost of ownership data from prospective and actual customers. The following are two case studies where AEDI has been successfully demonstrated.

One of the first installed AEDI systems was in PCB, close-looping of a board cleaning line. Savings from installed systems have met or exceeded customers’ expectations, by allowing the customer to eliminate the cost of systems. From this data, it is clear that the total cost of ownership of a company system is better than the cost of competing systems, driven by the effectiveness delivered by company product.

The purpose of the lines is to provide a clean inner layer core of the PCB and coat this core with a dry film resist. The facility was burdened with increased water and sewer costs due to the high usage of water and wastewater discharge. The plant was also subject to certain capacity limitations, which will limit future expansion and operating expenses.

AEDI provided high quality D.I. water for the lines since 2003, until the facility was shut down in 2014. The process lines demanded 16 gallons per minute (gpm) of continuous D.I. water supply. There were savings in city water and sewer charges, wastewater treatment and operating cost to the customer for the AEDI rinse water recycling system.

The water quality produced by the system was monitored for a period of 24 months by the customer to assure consistent and reliable quality.

The AEDI membrane modules are designed and built to ensure the purification of low TDS process water instead of using a mixed-bed ion ex-change system. A TDS reduction to more than 99% has been accomplished consistently and the product water is of D.I. water quality.

The diagram above shows the consistent high water quality produced by the AEDI which was installed over 40 months ago. Figure 2 shows a summary of this data for about 36 months of operation.

Disk Drive Cleaning System Case Study

Precision cleaning systems like the example shown in Figure 3 are used extensively in the tech production industries such as disk drive industry and PCB industry. In this particular cleaner, parts undergo a multi-step cleaning process. Parts are initially placed in a surfactant bath and subjected to ultrasonic waves, which form cavitation bubbles. The formation and collapse of the cavitation bubbles effectively scrub the many faceted surfaces of the mechanical parts. After the surfactant bath, the parts are sprayed with clean DI water and placed in progressively cleaner DI rinse baths. The DI rinse baths subject the parts to more ultrasonic waves and a continuous flow of clean DI water. After the last DI rinse bath, the parts are dried and taken to the production line.

Most precision cleaning systems rely on ultrasonics, but the individual baths are commonly aqueous based. The aqueous baths are either water plus surfactant based or simply (ultra-pure) DI water.

The following case study is based on data collected in 2014 and 2015 from wet processing involving the cleaning of disk drive in in-line cleaning operations. The point of use recovery system was tested and validated to meet the facility’s ultrapure specs, thus allowing for the water to be re-used and recycled in-line. The pilot system was operated for several months, so the data presented below is only a brief snap shot of the test results.

The base platform used for the application utilized the AEDI technology, plus a pre-filtration unit for the removal of organics, and particle removal and disinfection elements to address particle and bacteria formation in a closed-loop set up.

A system was installed and started up in mid-2014. The data shown in Figure 4 was collected over a period of three months for Phase I of the project, which involved the removal of cleaner solutions from the rinse waters while recycling back the water to processes. The cleaners contained a number of organic acids. Figure 3 shows a summary of the test results for resistivity in and out of the system for a period over 3 months.
As can be noted, the system was able to produce UPW grade (18 megohms.cm) recovered water for reuse.

Conclusions

AEDI in process rinse water recycling offers online, real time impurity removal and consistent high purity water for rinsing applications in the PCB sector. The technology has been validated and approved by customers with much higher water quality specifications such as in the disk drive industry and several systems have been successfully installed in the PCB industry.

The AEDI point of use recovery approach allows customers to reduce water usage by process and reduces water related operational costs.

Figure 2 – Case Study – PCB Line

Figure 3 – Parts Cleaner System
Figure 4 – Resistivity in and out during 3 months