Novel Waste-Treatment Technology Applicable to Aqueous Based Effluent Streams from Alternate Cleaning Processes to Facilitate Compliance with Environmental Regulations

By Jeff Spira

1.0 Introduction

Whether the PCB assembler cleans with aqueous (water based) or semi-aqueous (soluable organic solvent and water combination) solutions, all post wash cycle rinsing must be performed with deionized, high purity water. Wash solution recycling is a relatively simple affair, the solution being reused and refreshed until it is spent then disposed of as hazardous waste. Rinse water recycling is far more difficult since the sheer amount of water used is higher and the required cleanliness of the rinse water is much higher. Several existing technology methods are available for the post use treatment of the rinse water. These systems, though effective, can create additional environmental problems. The new technology presented in this paper solves these problems and offers a low initial, low operating cost viable method for fully recycling the rinse water.

The process of reuse of water used for the rinsing of PCB assemblies requires the removal of both organic and inorganic contaminants from the water. The organics consist of soldering flux remains, dragout from the defluxing chemicals, products of the wash chemistry, (such as rosin soap created in the rosin/saponifier reaction) and any remaining oily contamination on the PCBs following the wash cycle. Inorganic materials remain in the rinse water created from the same sources. The inorganics are primarily in the form of dissolved minerals and salts, i.e. ionic contaminants.

With existing technology, these two very different contaminant types, organic and ionic, must be removed with very different chemical methods. Organics removal from water does nothing to remove any dissolved inorganic contaminants. While the mechanical inorganic removal methods, Reverse Osmosis (RO) and microfiltration, are capable of removing organics, the presence of organics fouls the membranes or filters rendering mechanical methods unsuitable. In addition, the use of microfiltration and reverse osmosis methods creates a high purity stream and a reject stream. The reject stream is roughly half of the incoming water volume. Thus, there is a requirement for makeup water since only half of the water is reusable. In addition, the mechanical method succeeded in only concentrating the hazardous waste creating a less expensive disposal problem, but doing nothing to eliminate the problem.

A workable system would be required to have the organics removal upstream of the inorganic removal omponent. This would allow the use of inexpensive and proven inorganics removal methods.

2.0 Organics Removal

2.1 Traditional Methods

The traditional method to remove organics from water is by adsorption via activated charcoal. The process requires an extended exposure time of the water in the charcoal such that the heavy molecular weight organic compounds are trapped in the very porous structure of the carbon. Granulated Activated Carbon (GAC) filters are sized for a flow calculated to expose the water to the granules of carbon long enough to remove the expected amount of organics in the water. The vast majority of commercially available GAC filters are designed for use in potable water systems, where the amount of organic contaminants in the incoming water is low. They prove effective for this potable water application.

The use of GAC filtration for industrial process water raises other problems. Rinse water from PCB defluxing is much higher in organics than would be expected from a potable water source. The sheer amount of GAC required to get an adequate contact time compatable with the required flow rates is excessive. The carbon requires frequent changing due to adsorbed organics loading. This is not as big a problem as it may seem since the cost of GAC is relatively low. It does present a regular maintenance expense both in labor and in new GAC with the associated process down time while the maintenance is being performed.

Different organics present in the water have different adsorption rates. This means sizing of the GAC system for the expected flow rate and expected organic chemical loading in the waste water is critical. In many cases, the volume of GAC required is much higher than the anticipated to achieve the required contact time if a particularly difficult to adsorb organic chemical is present in the waste stream.

The spent GAC presents disposal problems. The porous material having adsorbed all of the volatile organic compounds (VOCs) is now considered hazardous waste. GAC can be recycled by steam cleaning to remove the organics, but these must then be disposed of properly. Some areas permit incineration of the VOC loaded carbon, but this, too is an environmentally questionable solution.

2.2 Chemical Conversion of Organics

The most effective method of removing the organic contaminants is to fully oxidize the organics in solution. This chemically converts the VOCs to benign Carbon Dioxide, water, and metallic oxides. These are ionic rather than organic contaminants. The Carbon Dioxide is readily outgases off the solution, the water is a desirable addition to the solution, and the metallic oxides are readily removed by ionic removal means.

All organic materials, whether a result of fluxing, the drag out from semi-aqueous solvent mixtures, or from oil and grease contamination, are in the form of hydrocarbons; predominantly carbon – hydrogen compounds with small amounts of other chemicals. The hydrocarbon oxidation reaction is as follows:

$$C_{X}H_{Y} + O_{2} => CO_{2} + H_{2}O$$

Since all alcohols, oils, terpenes, other petroleum and limonene based materials fall into the $C_x H_y$ or $C_x H_y O_z$ compounds, the oxidation reaction alone is sufficient to fully decompose these materials into Carbon Dioxide and water.

Simply using molecular Oxygen (O_2) this reaction rate is too slow to be of significant use in a production environment. The reaction rate may be stepped up greatly by using Ozone (O3) as the oxidizing agent.

Ozone is produced naturally in the environment by the action of high energy radiation on molecular oxygen. This is done in the upper atmosphere with solar radiation and in the lower atmosphere with lightning. The formation of Ozone is as follows:

$$3 O_2 + ENERGY => 2 O_3$$

In addition to natural methods, Ozone is also readily made from Oxygen in the air by several methods. Significant quantities may be manufactured from air in a short enough duration of time, with low power requirements to make it a practical substance for oxidizing the amounts of organic contamination typically found in PCB rinse water.

Ozone is also highly soluble in water. Its rapid dissolution property and highly reactive nature make it a nearly ideal agent for the oxidation of organic contaminants.

A properly designed machine using an Ozone generation and dissolution method is both practical and economical for production removal of organics from water. The process is inherently non-polluting since the by products of the reaction are simply Carbon Dioxide and water. Another advantage of this system is the lack of any consumable or regularly maintained additives. The input is simply air and power, while the output is air with a slightly higher CO_2 content.

3.0 Ionic Contaminant Removal

3.1 Traditional Methods - Resin Ion Exchange Systems

Dissolved mineral and salts in water disassociate into ions, that is, electrically carged atoms and molecules. The cations (positively charged) consist of the metallic elements predominantly Sodium, Calcium, Iron, and Magnesium. The anions (negatively charged) are the Oxides, Carbonates, Chlorides, and others.

Traditional ion exchange systems utilize a two-stage process, a cation exchange bed and an anion exchange bed, Ion exchange resins are made up of spherical grains of polymers designed specifically as cation or anion resin. The figure below illustrates their operation.



In the cation exchange bed, the resin is recharged with acid. The free ionic Hydrogen of acids accumulate on the surface of the resin. As water passes through the resin, the cations attach themselves to the resin and are exchanged with the ionic Hydrogen as shown.

In the anion exchange bed, the resin is recharged with a strong base. The alkaline with its free Hydroxyl radical attaches the IH to the resin. As the water passes through this bed, the anions are exchanged for the Hydroxyl as shown in the preceeding figure.

The effluent from the cation exchange bed (H) and from the anion exchange bed (OH) combine to form water as follows:

$$H^+ + OH^- \Longrightarrow HOH = H_2O$$

All dissolved minerals are removed and exchanged for the constituents of water. This creates high purity water.

Ion exchange demineralization of water is not a new process or technology. It has been successfully used for many years. Likewise, its shortcomings are well known and documented. For instance, following use, the exchange beds must be recharged. A method to shut down the water system to introduce highly corrosive concentrated acids and highly caustic bases into their respective resin beds must be incorporated into the system. These corrosive chemicals must also be stored and handled. In addition, the recharge process strips the resins of the removed ions. Disposal of this high concentration, contaminated water also presents some problems. It is far higher in dissolved solids than is permitted in many communities for disposal in the POTW sewer system.

Some manufacturers try to avoid the regeneration issue by simply changing resin. This does not solve any problems since the resin must still be disposed of properly or shipped to a facility for regeneration. It seemingly shifts the responsibility for the problem, but the generator of the waste never really loses responsibility for it.

Though effective, the use of ion exchange deionization presents significant chemical storage, handling, and disposal problems. Though the operating costs are low, the regeneration or resin replacement costs are high. This makes it impractical except for very low volume systems, infrequently used with low contamination levels. It is not a practical approach for simple, low cost production equipment.

3.2 Electro-Deionization

Electro-deionization (EDI) is a relatively new technology system designed to remove dissolved minerals from water. The system utilizes ion exchange resin in a totally different way to concentrate the ions into a reject stream and fully deionize the product water.

They system operates as follows: Feed water containing ions is introduced into a chamber containing mixed anion and cation exchange resins. The resins are retained between an anion permeable membrane and a cation permeable membrane. A DC electric field is charged on the bounds of the membranes. The dissolved anions are attracted to the positively charged terminal due to the electrical attraction of positive and negative particles. These anions pass through the anion permeable membrane and into the waste stream.

In a like manner, the cations are attracted to the negatively charged terminal and pass through the cation permeable membrane and into the waste stream. This figure illustrates this exchange.



The efficiency of EDI is typically over 90%. The feed water passes through and is deionized to a high purity. The reject stream, less than 10% of the total flow, contains all of the ions and may be disposed of or reclaimed by distillation leaving inert salts.

4.0 A Machine To Recycle Rinse Water

The combination of these two new technologies, Ozone organics oxidation and electro-deionization applied to rinse water produce a DI quality effluent capable of being reintroduced into a cleaning machine. Hence, the system can be made totally closed loop.

If a distillation system is added to reclaim the waste stream for the EDI, the only makeup water required is to account for the small amount of evaporation. This water may be added as tap water introduced into the oxidation reaction vessel. The Ozonation and EDI will remove any contaminants in the tap water. The only pretreatment required is the removal of bacteriostatic Chlorine normally added to city water for sterility. The Ozone system will maintain a high state of sterility of the water and system after the Chlorine has been removed. An absorptive GAC filter can be used for the de-Chlorinization function. The minimal amount of made-up water required will allow for a long usage of a small cartridge type GAC filter.

The schematic shown in figure 3 shows the Ozonation/EDI system complete with distillation of EDI waste stream reclamation. The only required maintenance would be the semi-annual replacement of the de-Chlorinization GAC cartridge and the annual cleanout of the distillation chamber. The organics will be totally broken down into CO2 gas and water, while the ionics will be removed as a benign solid scale. The system will only require electrical power for the pumps, heaters, Ozone generation unit and EDI.

Controls for the system are minimal. A water quality monitoring system is used to operate the EDI polishing loop. Simple float switch controls are used to pen the makeup water valve and start and stop the distillation unit.



Complete Closed Loop Purification System