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# PRETREATMENT GENERAL SESSION

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## Closed Loop Aqueous Washing

*Electroplaters have long realized the benefits of minimizing wastewater and closing the loop on their finishing operations. However many companies involved in pretreatment and parts washing spent most of their available resources on the equipment and process concerns of the transition from solvent to aqueous processes. Now that many of these concerns have been addressed, thoughts are now switching to environmental considerations. Methods used in plating to purify process baths, recover chemicals and conserve water can be applied to cleaning and pretreatment baths. This paper will explore the equipment and chemistries available to minimize waste and present a method to close the loop on aqueous cleaning operations.*

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## Closed Loop Aqueous Washing

Vapor degreasing utilizing chlorinated solvents was once the gold standard for industrial cleaning. Vapor degreasing is independent of the base metal, it removes oils and greases efficiently, it works quickly, and parts emerge from the operation dry. The cleaning solution was easily recovered as a purified liquid leaving only a small volume of residual oil for disposal. Unfortunately vapor degreasing, uses solvents that deplete the ozone layer and the US EPA decreed that industry would no longer be able to emit these solvents into the atmosphere, generating a rush to aqueous cleaning.

### Challenges of Aqueous Cleaning

In many cases the process of aqueous cleaning was foreign to manufacturers. Since water is used as the solvent, issues such as part drying and the quality of the water quickly became important. Cleaner salts remaining on the work were unacceptable and the disposal of rinse water became an issue. Equipment used for solvent cleaning was usually not adaptable to aqueous methods and replacement equipment required more floor space. Many of the available cleaning products contained hazardous ingredients and shops were not set up to handle them. Discharges from aqueous cleaning systems are subject to various governmental regulations and permits are usually required for industrial water discharges.

### Waste Reduction

Many new government and industry standards, typified by IS0 14000 are requiring industry to employ technologies to reduce or eliminate the volume of waste and wastewaters generated through their manufacturing operations. Companies are finding competitive advantages in waste reduction.

Recently there has been considerable success in the reduction of wastes from aqueous cleaning operations through the combination of filtration and evaporation. This paper will explore the combined application of filtration techniques and evaporative recovery as it applies to aqueous cleaning.

**Aqueous Cleaning Mechanics**

Let us first start with a review of the aqueous cleaning process and chemistry. Manufactured parts are cleaned in a machine with an aqueous solution containing a detergent. The parts are then rinsed with a volume of fresh water to remove the detergent film. This machine adds thermal energy in the form of heat to melt waxes and grease and to accelerate the chemical action. Mechanical energy brings fresh solution into contact with the surface of the part and flushes away the dirt and oil from the surface. Chemical energy is supplied by the cleaner chemistry including alkalinity for saponification, surfactants for oil removal, and sequestrants for water conditioning and preventing soil redeposition.

**Water Quality**

The quality of the water used in cleaning equipment is often ignored unless there is a requirement for a spot free surface after drying. Only then is DI water used, but just in the final rinse. When the pH is too far from neutral highly finished parts can quickly stain, chlorine from city water supplies can accelerate this problem. But the most damaging water ingredient in cleaning are the collection of minerals known as hardness. Water hardness consumes the expensive chelants and sequestrants in the cleaner and inhibits the action of the surfactants. Manufacturers who use chelate free cleaners can expect to find scale on the heating coils and sludge in tank bottoms unless DI water is used throughout.

**Typical System Operation**

Parts emerging from the aqueous cleaner carry with them a layer of the cleaning solution that needs to be rinsed from the surface. As the cleaner becomes contaminated with dirt and oil, cleaning times may increase and greater quantities of rinse water must be used to obtain acceptable parts. This continues until the cleaner has reached the end of its useful life.

**Cleaner Life**

All cleaners have a useful life span before they need to be renewed. This is the point at which the soil concentration being held by the cleaner overwhelms the ability to hold additional soil or prevent its redeposition. Then it is time to dump the cleaner and make up a new bath. Each time a new bath is made up, there is a large volume of contaminated water for disposal. Some cleaning operations purge soils from the tank the natural way, through dragout. High volume operations can dragout over 5 GPH. At this rate a 400 gallon cleaning tank would be renewed every two weeks. However this method results in the loss of large quantities of usable cleaner along with the soils and requires volumes of rinse water to prevent spotting. We have a situation involving complex chemistries, kept in balance by dumping or dragout and frequent replenishment. We are removing soils from the cleaner by disposal of large volumes of liquids. It would be much more sensible to remove just the soils from the cleaner and recycle any dragged out cleaner back to the original process. This is the situation we are addressing when we propose to use a system of filtration and evaporation to close the loop and recover the cleaner. For us to be successful we must:

1. Filter out the soils, saponified products, and floating and emulsified oils while leaving behind the detergent builders, sequestrants, and surfactants.
2. Recover the cleaner chemistry lost to dragout by reducing the volume and providing space for fresh water flow to provide adequate rinsing.

**Filtration Methods**

Let us first look at the available methods for filtration of aqueous cleaners and their effectiveness on each type of soil removed in aqueous cleaners. The most common filtration methods available involve the use of coarse screens, throw away cartridges, coalescers and skimmers, carbon, and membrane filtration.

**Screens**

Screens are the coarse filters typically constructed out of stainless steel and placed in line to remove the large particulate contamination. The mesh size of the screen is in the range of 50 to 500 microns or larger.

**Disposable Element**

Disposable element filters are represented by indexing belt and cartridge filtration methods. Indexing belt filters use a mesh belt covered by either cloth or paper filter media from a continuous roll. Dirty cleaner passes through the filter by gravity and is returned to the process tank. As the filter media becomes clogged the solution level rises and the filter media is indexed to expose fresh media. Cartridge filters use either a porous solid or wound tube under pressure. Once the tubes are clogged they are thrown away and fresh tubes are installed. These methods are effective for shop dirt, fines, and some soluble oils but the filter media is added to the volume of waste that needs disposal.

**Coalescers/Skimmers**

Coalescers are effective devices at removing large amounts of floating insoluble oils, such as those used in cold heading and on screw machine parts. The quiet zone and long flow path allow mechanically emulsified oils to separate and float on the surface for removal. Coalescer oil removal effectiveness is 75 to 95% of the insoluble oils. The disks or belts on the skimmer extend into the floating oil layer, removing a portion of the oil that clings to the surface and is squeegeed into a drum for disposal.

**Carbon**

Carbon filters can absorb oils and organic solvents. They have a limited capacity and maintenance may be costly In addition to the contaminants they can also remove the active sa-factants from the cleaner thereby lowering the performance.

**Membrane Filtration**

The types of membrane filtration considered for aqueous cleaners consists of Microfiltration, Ultrafiltration, and Reverse Osmosis. These filtration methods are closely related in their methodology differing mostly in the porosity range used. While microfiltration has the largest pore size and reverse osmosis has the smallest, there is overlap between the methods at their limits.

Membrane filtration differs from the prior techniques discussed as it uses a crossflow process. The solution is pumped across the membrane surface at high flow rates and pressures rather than forced or sieved through a porous membrane. The membrane filter barrier can be thought of as a molecular filter. Solid and dissolved particles of greater molecular size than the membrane pores are swept along with the solution flow and concentrated as retentate. Water and dissolved chemicals smaller than the pore size pass through the membrane as permeate. The membrane size in crossflow filtration ranges from about 1 micron with microfiltration to one ten thousandth of a micron with reverse osmosis.

**Microfiltration**

Microfiltration is generally thought of as filtering with a porosity range of 0.8 to 0.05 microns. At this level of porosity both mechanically and chemically emulsified oils are retained on the concentrate or retentate side of the membrane. . Fatty acid soaps from removal of buffing compound and many of the newer synthetic coolants also are retained here. The detergent builders and surfactants pass through the membrane with the water and are available for reuse. Not all of the surfactants pass through the membrane as permeate. Surfactants are often tied up with the oil and soils that they remove. These “used” surfactants that have combined with other materials are also left behind with the retentate. The permeate is returned to the tank as purified product for reuse.

**Ultrafiltration**

Ultrafiltration has a tighter pore size than microfiltration, the range being 10 to 2000 Angstroms. An angstrom is one ten thousandth of a micron. With this pore size, emulsified oils don’t stand a chance of passing through the membrane. Unfortunately many of the synthetic detergents or surfactants are of a large enough size such that they are unable to pass through the membrane. This membrane will allow the detergent builder to pass through but by stripping the surfactants along with the oil the cleaner life is shortened.

**Reverse Osmosis**

Reverse Osmosis has the tightest pore range of the membrane filtration used in metal finishing. The pore size is ten Angstroms and below. At this level of filtration both organic and inorganic components of the cleaner are stripped. The application of RO is more suited to pure water requirements than purification of cleaners, as the permeate produced is high purity water and the retentate contains all the cleaner components including the dirt and oil. RO membranes are more sensitive to oil fowling than those used in UF and Microfiltration.

From this discussion we can see that microfiltration offers the greatest opportunity for cleaner purification.

**Microfiltration Membranes**

Currently there are three basic types of membranes being offered for microfiltration systems.

- Polymer types such as polysulfones and polypropylene are popular due to their low cost. However their operating temperature is limited to approximately 110°F. Solvents even in trace amounts may also damage the membranes irreversibly by swelling them shut. The cleaning methods available for fouled membranes are limited as strong chemicals can damage membranes.

- Ceramic membranes typically have a sintered metal membrane such as zirconium or titanium oxide over the support structure of an aluminum oxide tube. The cost of this type of membrane is intermediate to the polymer and graphite ones. The amount of sintered deposit controls the porosity. Ceramic membranes have high temperature tolerance and the ability to be backwashed with mild acid or caustic. However strong acids or caustics can attack the ceramic support.

- Carbon/graphite fiber tubes use a sintered carbon membrane surface for microfiltration. These membranes can be tailored to varying porosity's by varying the sintering temperatures and chemistries. The cost of the carbon/graphite membrane is greater than the other commonly used membranes. However they offer the advantage of high temperature resistance with the ability to be cleaned with strong acids and hot caustic solutions. This ability to be regenerated over a long period of operation typically brings operating and maintenance costs below that of other membrane systems.

**Microfilter Application**

Microfiltration systems can be designed and scaled to process the entire cleaning bath through multiple passes, with the main objective being to maintain the cleaner as close to zero oil content as possible. However when one considers that cleaners are designed to hold certain amounts of oil effectively, a smaller and more economical system may be designed which maintains an acceptable level of contamination.

The recommended system includes a particulate filter for solids and a coalescer for non-emulsified oil. The emulsified oils along with the emulsifiers and wetting agents tied up with the removed oil are removed by the microfilter at a rate that allows the cleaner to maintain a healthy ratio of virgin to spent emulsifiers and wetting agents, extending its effective working life by many times. The cleaner is not kept in a pristine state, which would require large membrane surface area and high solution flow possibly stripping active synthetic detergents. Typically a cleaner that would be replaced on a weekly basis without microfiltration, will function effectively over a period of three to eight weeks.

Rinsing operations following cleaning are also improved through the use of microfiltration. Since floating oil has been removed and emulsified oil maintained at nominal levels, less water is needed for rinsing.

Cleaners are often used at higher concentration levels than needed at initial make-up. This is done to provide a reserve for cleaning as soil loading increases. A cleaner maintained at low levels of soil loading can function at lower concentration levels, needing less water to rinse the cleaner salts from the work. Many chemical suppliers provide their detergents with a separate synthetic detergent package. This can be especially advantageous as only the components of the cleaner used in oil removal need to be replaced rather than the full blend.

The microfiltration techniques described can extent the life of a cleaner bath 3 to 10 times that of its unfiltered counterpart. Where cleaners are dumped on a weekly or bi-weekly basis the savings in make-up and hauling costs can be significant. There are also substantial benefits for plants with their own waste water treatment systems. Cleaners are formulated to suspend and disperse solid particles and to chelate metals to keep them from redepositing. This is in direct opposition to the reactions desired in waste water treatment. It is no wonder then that cleaners cause the most problems and greatest potential for upset in the best run treatment systems. Even in systems fully equipped to handle cleaner dumps on a regular basis, the volume of sludge generated is quite high for the volume of liquid and the sludge formed is resistant to filtration.

But even if we obtain infinite cleaner life, and never have to dump a cleaner there is still the factor of dragout of the cleaner to the rinse tank. Detergent dragout can range from .5 GPH to over 5 GPH. With cleaner make-up costs of $.50 to $.75 per gallon, there can be $ 30/shift worth of cleaner passing to drain, not even considering treatment costs.

## Evaporative Recovery

The lessons learned from electroplating bath recovery can be applied to detergent baths. Evaporation can remove water from the effluent, concentrating valuable salts for recycle.

Most cleaners are operated at elevated temperatures. This leads to a natural evaporation from the cleaner tank based on solution temperature, surface area, and air flow over the tank surface. This rate can vary from a couple of gallons per hour for a still tank with low air flow to over 10 GPH in a spray washer with an effective exhaust system. Since oil and dirt are now being removed constantly from the cleaner tank with microfiltration, the material dragged out is suitable for reuse. Rather than using fresh water to replenish solution evaporation, the rinse with dragged out cleaner is employed. This simple method can recover a small amount of the total dragout, but does not flush the rinse tank sufficiently to eliminate water flow. The solution to this is the use of forced evaporation on the rinse tank to remove 30-40 GPH of water and concentrate the rinse for reuse in the cleaner tank. This will provide sufficient flow to rinse parts free of significant cleaner residue in many instances.

## Types of Evaporators

There are many evaporators on the market. The most commonly used evaporators used in metal finishing are Boiling type, Vacuum, and Atmospheric.

## Principles of Evaporation

Before we discuss the types of evaporators, let's review some of the principles of evaporation.

- Heat is required for converting water from the liquid state to the vapor state. Whether in a vacuum or under atmospheric pressure it still takes between 900 to 1000 BTU's to convert one pound of liquid water to steam. So whether water is evaporated at 90°F in a vacuum evaporator, at 140°F in an atmospheric evaporator, or at 212°F on a boiling evaporator the same amount of BTU's are needed. Don't be fooled by claims that the evaporator can use the heat from the heated tank for evaporation. Unless the process generates sufficient excess heat to provide the BTU's needed for the phase change, the process will suffer.
- A means must be provided to remove the vapor generated by evaporation. There is a tremendous volume increase in the conversion from liquid to vapor. Unless means are provided to remove this vapor and prevent the condensation into the liquid tank, efficiency will suffer. Pay close attention to the design of systems that vaporize and condense in a closed system to assure that there is sufficient condenser capacity to prevent the circulation of humid air and water vapor.
- As the solution being evaporated becomes more concentrated with salts, more heat is required to maintain a given temperature and the evaporation rate. There is a practical limit to the salt concentration where the evaporation rate will suffer. Concentrate needs to be withdrawn on a regular basis to maintain efficiency.

## Boiling Evaporators

Boiling evaporators are low to moderately priced tanks with an exhaust vent. Heating may be by electrical resistance immersion elements, or direct fired immersion gas tubes exhausted to the outside. They operate at the boiling point of the liquid, 212°F for pure water to 230+°F for concentrated solutions. Many cleaners contain surfactants that will break down at these temperatures, so that the recovered solution has little value. When this type of evaporator is used with solutions that contain oil, there are additional concerns. Floating oil can form a blanket that seals the surface of the solution and retards evaporation. If additional heat is applied, steam may form under the oil layer, and the rapid expansion can spatter oil large distances. Even more serious is the possibility of ignition of the spattered oil on units that use direct gas fired burners.

**Vacuum Evaporators**

Vacuum evaporators have the highest capitol cost of those being considered today, however they will provide high purity distilled water for reuse in the process or other areas of the plant. Vacuum evaporators operate at low temperatures, protecting heat sensitive ingredients and providing comfortable surrounding temperatures for area workers. Vacuum evaporators are fairly complex pieces of equipment, requiring skilled operators and maintenance personnel.

**Atmospheric Evaporators**

Atmospheric evaporators operate in a manner similar to a cooling tower. They are low to moderate in capitol cost and will usually operate in a temperature range of 140-150°F, which is in the same operating range of cleaners. Since the solution is drawn from the bottom of the tank and sprayed through the air flow, floating oil has little effect on the operation. An atmospheric evaporator must incorporate an integral mist eliminator to catch any water droplets entrained in the exhaust air. Heating is through the use of hot water, electric, or steam so that the flammability of the oil is not an issue. The maintenance and operation of an atmospheric evaporator is fairly simple with components familiar to most maintenance personnel.

**System Operation**

With evaporative recovery added to microfiltration, we have virtually closed the loop on parts washer operations. (See figure #1)

Evaporation may be further used once the cleaner reaches the end of its useful life. At this point the cleaner and all the rinses are pumped to the evaporator over the weekend to reduce the volume of waste for disposal to a minimum.

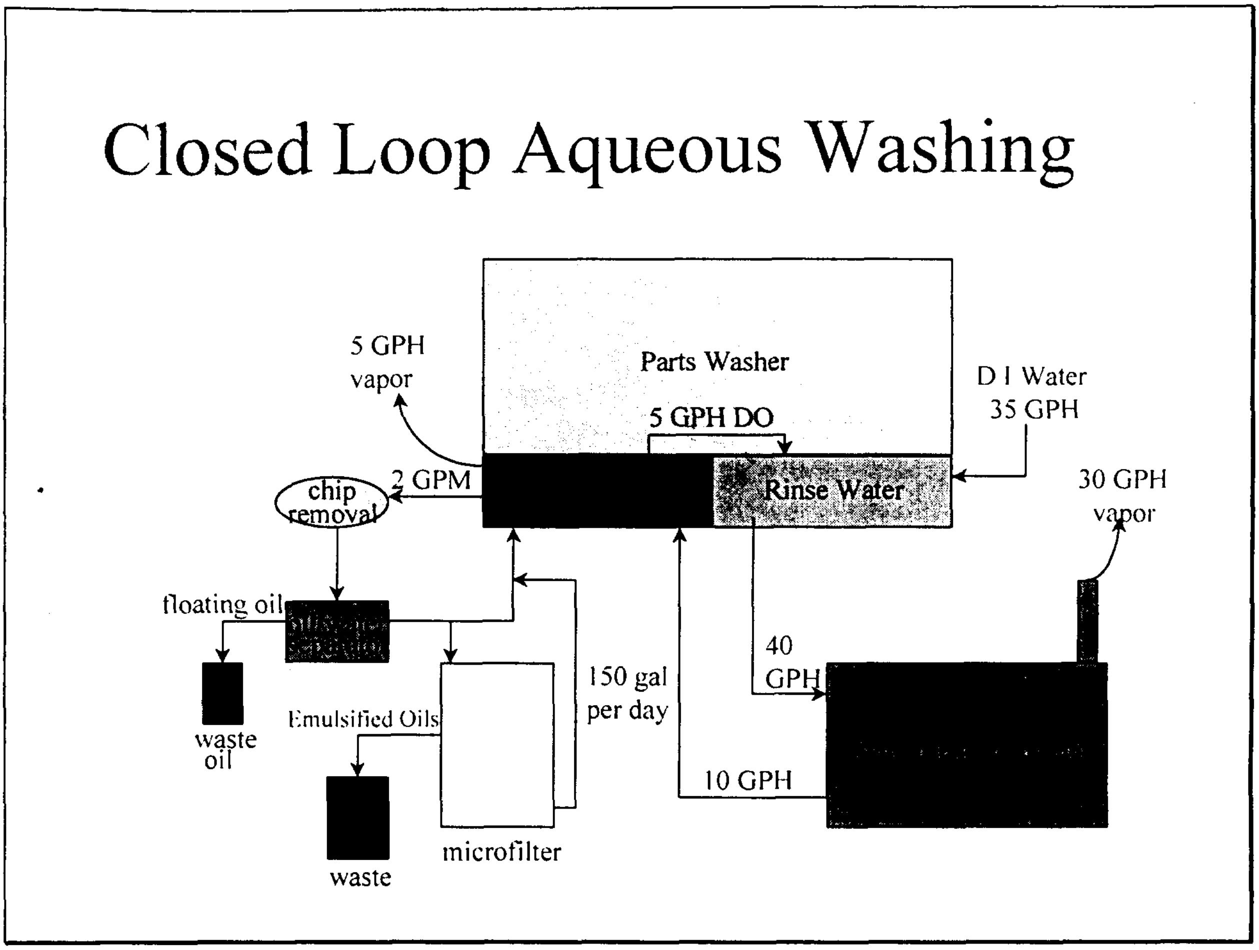
**Closed Loop Benefits**

Microfiltration and evaporative recovery offer practical methods of closing the loop on aqueous cleaning operations. However since each application presents a unique set of circumstances, the manufacturer should carefully investigate carefully before investing. It is advisable to bring the supplier of your detergent chemistry on board to offer alternate chemistry to enhance the recovery process. Often recovery can make higher performance products more affordable, improving manufacturing processes.

Additional benefits of closed loop operation are:

- Elimination of environmental compliance issues. With no discharge, sewer regulations, inspections, discharge permits and permit violations are a thing of the past.
- Waste reduction is an important part of IS0 14000 compliance
- Reduced disposal volumes can place you in a lower discharge category
- Reduced chemical purchases will lower your costs.

The value of these benefits make it worthwhile to expend the effort to properly design and operate these systems in your operation.

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Dick Heller is a sales engineer for Aqualogic Inc. in North Haven, CT. He received his degree in chemical engineering from the University of Connecticut. Mr. Heller has worked in metal finishing his entire career, including a high volume captive shop where he installed and operated waste water treatment and recovery equipment. His most recent experience was as technical director for a metal finishing supplier formulating aqueous cleaners. Mr. Heller has been active in the technical societies including the AESF and MFSA, serving on various boards and committees.