



NEW YORK STATE

POLLUTION PREVENTION INSTITUTE

Metal Finishing Processes



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Plating or Conversion Coatings

Overview of plating or conversion coating

Plating is the application of a metal or metals to a substrate, the typical substrate being metal. A typical line will be dedicated to a specific base metal and a specific plating. For instance, a plating line may be designed to plate steel parts with a layer of copper followed by chrome. Since plating is being applied to the part, the part dimensions will change in a direct relationship to the amount of plating applied.

Plating can be applied either with or without the use of electrical current. For example, there is nickel plating which requires electric current to force the nickel to plate out on the parts and there is electroless nickel plating which will plate out spontaneously but slowly without the application of an electric current.

The conversion coating process is a coating created on the surface of a metal part due to the reaction of the metal surface with a chemical. Examples of conversion coatings are phosphate, chromate, black oxide, and iridite on aluminum. A special type of conversion coating is anodizing and will be discussed later. A part that has a conversion coating will have dimensional growth that is proportional to the conversion coating thickness but is not a direct relationship as in plating. This is because the conversion coating is consuming some of the substrate metal in the process of forming the coating. A conversion coating is growing into the part as it is formed but is also of greater volume than the original metal. Therefore, it both grows into the part and expands as the coating forms.

Typical steps associated with both plating and conversion coating:

1. **Alkaline** Cleaning (typically an alkaline chemistry)
2. **Rinsing**
3. **Acid Etching and Acid Cleaners**
4. **Rinsing**
5. Plating or Conversion Coatings
6. **Rinsing**
7. **Part Drying**

Example of an automatic hoist plating line



Image courtesy of [Baker Technology](#).

Example of Black Oxide conversion coating on steel





Solution Recovery:

The method of either extending the life of a plating solution will be very dependent on the type of plating being done. The following is an overview of the technologies available to recovery or control various plating solutions.

Chrome plating:

There are three recovery areas from a chromium plating process tank.

1. Exhaust system

Mesh Pad Mist Eliminators in the ventilation system provide two advantages. First, they are very effective as the first stage in chrome mist removal. Second the back wash operation for the mesh pads allows the chromic acid to be recovered and returned to the plating tank.

2. Rinse tank

Since a chrome plating tank is typically heated and therefore losing volume due to evaporation, a stagnant primary rinse tank should be used for make-up solution to the chrome tank. In addition, a porous pot described below, can concentrate the chromic acid in a rinse tank for recovery.

3. Plating tank

Ceramic porous pots are one commercially available method of keeping the non-chromium metal contaminants to a minimum. The technology is the use of a ceramic "pot" as a membrane and the use of electrodes to pull the non-chromium metal ions into the pot while leaving the chromic acid ions in the tank. The pot is suspended in the chrome tank with its own rectifier to provide continuous filtration of the metal contaminants. One source of the porous pot equipment is Hard Chrome Plating Consultants, Inc.

Methods of plating solution recovery from rinses:

The goal in solution recovery is to put the recovered solution back into the plating tank in a form that will not negatively influence the plating or conversion coating tank chemistry.

Direct evaporative loss additions

The simplest method is to have a stagnant rinse tank for the first rinse and use this rinse water as make-up water in the process tank. This is particularly useful for hot process tanks since the process tank is regular need of water to compensate for evaporation. In the case of lower temperature process tanks with minimal evaporation, the rinse water containing process chemistry will need to be concentrated before being added back to the process tank. This can be accomplished off line with an evaporative system to concentrate the rinse water to the correct process concentration. Then the concentrate can be used as chemical make-up solution in the process tank.

One warning regarding introduction of process chemistry from rinse water is in the scenario where the dragout from the process tank to the rinse tank serves the purpose of removing process tank impurities. In this situation, the reuse of the recovered chemistry will shorten the



process bath life by reintroducing the impurities. The aluminum anodizing process is an example where the dragout losses from the anodizing tank include dissolved aluminum which tends to build up in the tank and needs to be removed anyway.

Ion Exchange

The purpose of ion exchange is to capture and concentrate the dissolved metals in a plating solution rinse. Once captured by the ion exchange resin, the metal can be removed during the regeneration process, concentrated by evaporation and returned to the plating tank. Again, there are potentially other chemicals in the plating bath which are not captured by the ion exchange (organics such as saccharin) and therefore need to be added to the plating bath to maintain the proper concentrations.

If the ion exchange regeneration solution cannot be used for plating tank additions, it may have high value for its metal content. Some companies such as Inmetco are very interested in metal recovery due to the value of the metal. Copper (\$3.81/lb), nickel (\$10.21/lb), and chrome (\$5.81/lb) all have relatively high market value (2010) and therefore are worth considering for scrap recovery.

Electrodialysis

Electrodialysis is very similar to diffusion dialysis in that there is a semi-permeable membrane that allows preferential passage of some ions while excluding others. The process of moving ions selectively across the membrane is accelerated by the use of electrodes beyond the membranes to help draw the ions through the membranes. This technology is typically used in nickel and electroless nickel plating to recover the nickel chemistry from the primary rinse tanks.

Reverse Osmosis

Reverse osmosis is typically used to concentrate the desired chemicals from a dilute solution. The process involves a membrane that is permeable to water and small ions such as sodium or potassium but not larger ions. Pressure is applied to the solution to force water through the membrane and leaving behind the chemicals of value. Plating solutions of high value can be concentrated from rinse solutions and recovered for reuse using this method. Plating solutions such as NiSO_4 can be recovered in this way.

Metal recovery from rinses

Electrowinning

Concentrated rinses can be sent to an electrowinning (electroplating) tank to plate out the metal which can then be sent out as scrap metal rather than being treated by other means. The wastewater from the electrowinning process will still need to be treated for metal but the metal content will be much lower and therefore cost less to treat and cost less for sludge disposal since the sludge volume will be much reduced.

Electrowinning is very common in precious metal plating since the electrowinning system can be installed directly in the rinse tanks and therefore keeps the precious metal concentrations very



low in the final rinses by keeping the concentrations low in the primary rinses. As a final precious metal recovery step, the final rinse can also be recirculated through an ion exchange system to scavenge the remaining precious metal in the final flowing rinse before the rinse goes to wastewater treatment.



Plating or Conversion Coatings with Anodizing as a Special Case

Overview of Anodizing

The term anodizing is typically used to describe the conversion coating applied to aluminum. It can also be used to describe conversion coating applied to titanium, magnesium, niobium, or tantalum parts. The difference between anodizing and a typical conversion coating is that anodizing is generated by a combination of both chemical conversion and electric current at the metal surface. The electrical current forces the anodizing layer to form both faster and thicker than it would by chemical reaction alone. Another aspect of anodizing is that the anodizing process leaves micropores in the coating which can be filled with dyes to produce a wide range of part colors.

Typical steps associated with anodizing:

1. **Alkaline** Cleaning (may be a modified alkaline cleaning to avoid pitting)
2. **Rinsing**
3. **Acid Etching and Acid Cleaners** (may contain fluorides to remove aluminum oxides)
4. **Rinsing**
5. Anodizing
6. **Rinsing**
7. **Dyeing** (optional)
8. **Rinsing**
9. **Sealing**
10. **Rinsing**
11. **Part Drying**

Porosity in an unsealed anodized surface

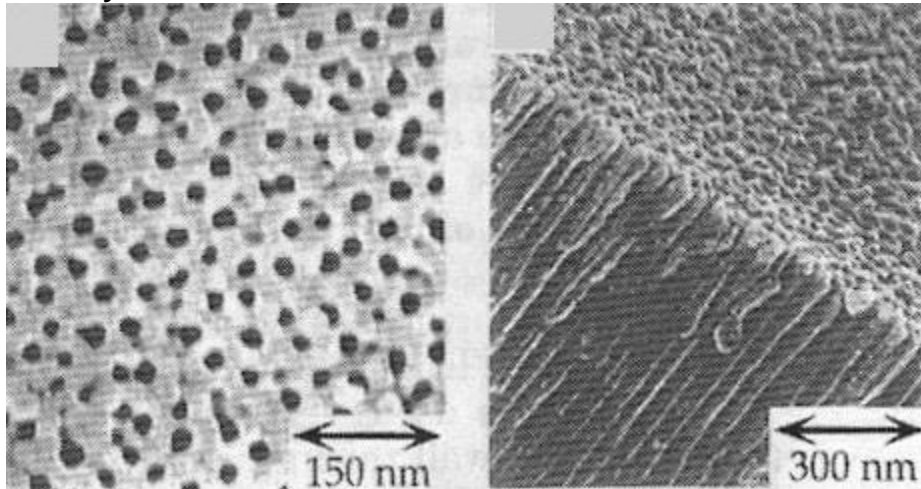


Fig. 6. Surface and cross section near outer surface of porous oxide (From T. Kyotani, L. Tsai, and A. Tomita, *Chemistry of Materials*, Vol. 8, p 2109, 1996).

Example of color capability in anodizing



Dyeing

The dyeing operation in anodizing is rather unique compared to other chemical process steps in metal finishing. Typically the dyes used are organic and can be sensitive to acid from the anodizing process or contaminants in the rinse water. Therefore, post-anodizing rinsing is critical before parts go into the dye tanks to avoid contamination of the dye tanks. The pre-dye rinse needs to be a high purity water rinse such as deionized water and room temperature or



cooler water. The use of a heated pre-dye rinse would begin to seal the pores in the anodized surface and could reduce the dye pickup into the pores.

Depending on the dye, air agitation is either required or forbidden. The dye manufacturer should be able to provide the best practices for their dyes.

The dyeing tanks are typically heated per the dye manufacturer's instructions. The warm dye is drawn into the pores of the anodized layer due to capillary action.

Sealing

The sealing operation is the final stage of the anodizing process. Immersion of an anodized part into hot (boiling point) water causes the pores to seal over due to the slight solubility of the aluminum oxide of the anodized surface. This provides stain and corrosion protection for a clear anodized surface and prevents dye migration or degradation in a dyed surface. The hot water used in sealing also needs to be high purity such as deionized water. Sealing additives are also sometimes used such as nickel acetate with boric acid. The use of additives requires additional wastewater treatment.

Solution recovery

Anodizing solution is typically sulfuric acid. A small amount of dissolved aluminum is helpful to the anodizing process. However, concentration limits are suggested by the manufacturers of specialty chemical mixes for anodizing. In *Aluminum How To, The Chromating-Anodizing-Hardcoating Handbook* by H. R. Probert, the author recommends concentrations no higher than 12 grams per liter of dissolved aluminum.

Methods of dissolved aluminum concentration control:

1. Decant and replace

A known amount of solution is removed from the anodizing tank such that an addition of the same volume of fresh acid will reduce the total dissolved aluminum to between 5 and 8 grams per liter. The acid-aluminum solution that is removed can either be purified off-line, disposed of as hazardous waste, or be used for other purposes in the plating area.

2. Diffusion dialysis

This process is able to control the aluminum concentration in the anodizing tank with the use of a selective membrane that allows sulfuric acid through the membrane while holding back the dissolved aluminum. Mech-Chem Associates, Inc. is one company that provides this type of equipment for acid recovery.

3. Acid sorption

The process of acid sorption is a resin column method of holding back the acid while allowing the dissolve metal to pass through. A back-flush of the resin with pure water allows the acid to be recovered from the resin and put back into the anodizing tank. The waste from this process will be high in dissolved aluminum and small amounts of acid. One company that manufactures acid sorption equipment is Eco-Tec, Inc.

Painting Process

Overview of Painting

The painting process is considered to be the application of a liquid organic coating to a substrate. Substrates can be plastic, wood, metal, ceramic, foam, paper, etc. The “paint” can vary from solvent based to 100% solids in the case of UV curing liquids. So the paint can be liquid due to various carriers such as solvents or water to a two-part epoxy paint or UV curing paint that cure by cross-linking rather than drying by the evaporation of the carrier.

The paint can be applied by various spraying methods such as electrostatic spray, high pressure spray, HVLP (high volume, low pressure) spray, etc.

Typical steps in a painting process:

1. **Alkaline** Cleaning (typically an alkaline cleaner)
2. **Rinsing**
3. **Phosphating** (optional step to improve corrosion protection and paint adhesion)
4. **Part Drying**
5. **Painting**
6. **Part Drying** (or **Drying** and **Curing**)

Example of electrostatic paint spraying, with very little overspray behind the parts



Image courtesy of [Products Finishing](#).



Electrophoretic Painting Process (E-Coat)

Overview of E-Coating

The E-coat process is best described as a cross between plating and painting. It is a process where a metal part is immersed in a water-based solution containing a paint emulsion. An electric voltage is applied to the part causing the paint emulsion to condense onto the part. A part can be painted both inside and out, wherever the liquid is able to reach a metal surface. The coating thickness is limited by the applied voltage. As areas of high voltage build a coating they become insulators thus allowing lower voltage areas to build up. Finally, the interior of a part can be coated since the exterior is fully insulated by the coating.

Following the painting tank, a rinse tank removes the residual emulsion from the part and recycles it back to the paint tank by ultrafiltration. The E-coat is cured by heat and the curing time and temperature is determined by the E-coat chemistry; epoxy, acrylic, etc.

The preparation steps for E-coat are identical to plating steps in that the metal surface must be chemically clean.

Typical steps in an E-coat process for metal parts:

1. **Alkaline** Cleaning (typically an alkaline cleaner, but substrate dependent)
2. **Rinsing**
3. **Acid Etching** and Acid Cleaners
4. **Rinsing**
5. Wetting agent dip
6. E-coat
7. E-coat rinsing and recovery
8. **DI Rinsing**
9. Curing with either convention or infra-red over (or both)

Wetting agent dip

Some E-coat manufacturers recommend a wetting agent dip in the tank immediately before the E-coat tank. This is typically to prevent bubbles from adhering to the parts as they go into the e-coat tank. Any bubble attached to the part surface will prevent E-coat deposition and will cause a paint defect in the finished part.

E-coat rinsing and recovery

An advantage to the E-coat process is the ease of recovering the E-coat that gets carried by the parts to the E-coat rinse tank. The E-coat rinse is constantly filtered through an ultrafiltration unit which separates the E-coat emulsion from the carrier solution and returns it to the E-coat tank. Most of the E-coat is recovered in this way.

Curing of E-coat

Since E-coat is essentially liquid paint once it has coated a part, it will require a curing cycle based on the type of paint chemistry being used. As an example, an acrylic-urethane type E-coat will require a curing temperature of 320 F for 20 minutes (metal temperature, specified for Electrocure 2800, product of PPG). As with paints, the energy used to cure the E-coat will depend on the part size and part geometry. Simple geometries may be able to be cured completely with the use of infrared heating since the infrared is line-of-sight and heats the metal surface without needed to heat the whole part. For complex geometries, a convection oven is typically needed to fully cure the E-coat in all areas of the part.

Since the E-coat chemistry can be a chemical cross-linking process, the full cure requires both time and temperature to obtain the optimum coating properties.

More information on infrared curing can be found in the powder coating drying and curing process description.

Extreme example of E-coating a complex part





Powder Coating Process

Overview of Powder Coating

The powder coating process is very similar to a painting process except that the “paint” is a dry powder rather than a liquid. The powder sticks to the parts due to electrostatic charging of the powder and grounding of the parts. Any substrate can be used that can tolerate the heat of curing the powder and that can be electrically grounded to enhance charged particle attachment. The powder flows and cures during the application of heat.

Several advantages of powder coating over paints are:

- Powder recovery for reuse
- No VOC generation therefore no VOC destruction required
- Can be more durable than paints (powder chemistry dependent)

Several disadvantages of powder coating over paints are:

- Can have less leveling than paint (more orange peel)
- Curing is typically more energy intensive than paint drying due to higher temperature requirements

Surface preparation before powder coat application is still critical for adhesion and defect avoidance.

Typical steps in a powder coating process for metal parts:

1. **Alkaline** Cleaning (typically an alkaline cleaner, but substrate dependent)
2. **Rinsing**
3. **Phosphating** (optional step to improve corrosion protection and adhesion)
4. **Part Drying**
5. Powder Coating
6. Drying and Curing (typically energy intensive since relatively high temperatures are required to get the powder to liquefy and flow*)

*Powder coating formulators have been working to reduce the cure temperatures to allow the process to be used on temperature sensitive materials.

Drying and Curing

The energy intensive operations in the powder coating operation are drying and curing. Typical drying and curing operations are with the use of convection ovens. The use of convection heating can be very slow and very costly if the parts are large and heavy since the evaporation or curing will be dependent on the bulk temperature of the part. Essentially the whole part must be hot enough to cause the part surface to either dry or the powder coat to cure. Therefore, large volumes of air need to be heated and exhausted from the convection oven to effectively dry or cure the parts.

This is much less of a problem for thin walled or low mass parts since the hot air can heat the parts relatively quickly with a resultant faster drying or curing process.

Depending on the part geometry, simple geometries can be dried and cured using infrared heating. The heating occurs at the part surface with little air heating or bulk heating of the part. Therefore, the heat energy is going where it is needed, to the surface. It is also a very rapid heating process, again since there is instant infrared light absorption.

Another advantage of infrared heating is in the powder coat curing process. The rapid part surface heating results in better powder flow and less chance of dust or dirt defects since there is very little air flow to deposit particles compared to convection heating.

As a side note, the use of infrared curing for liquid paints has an interesting and helpful effect. The infrared light heats the part surface and not the paint, resulting in paint drying from the inside out. The paint does not skin over and trap solvent or water inside the paint as can sometimes happen with convection curing. All the volatiles are driven out of the paint, starting at the part surface and progressing to the paint surface. You might say that the paint dries backwards.

Example of an infrared panel – in this case a catalyzed natural gas unit



Catalyzed natural gas IR emitter made by CCI Thermal Technologies

Example of a powder coating booth



Image courtesy of [Therma-Tron-X, Inc.](#)

Example of hand application of powder





Partial list of infrared equipment manufacturers:

- Casso-Solar
- CCI Thermal Technologies
- Fannon Industries
- Fostoria Industries
- Honesom
- Infasource Inc.
- Innovative Industries
- ITW-BGK
- Protherm
- Solar Products
- Thermal Designs and Manufacturing



Wastewater Reuse

Overview of Waste Water Reuse

Most metal finishing industries have in-house wastewater treatment to economically dispose of the acids, alkali, oils, and dissolved metals in the rinse water and occasional tank solution disposal. However, after treatment this water is typically sent to the sewer since there are still chemicals in the water which makes it unsuitable for reuse. The main post-treatment chemicals in the water are salts such as sodium chloride from the neutralization of hydrochloric acid and sodium hydroxide. Other residual chemicals could include soaps, chelating agents, or surfactants which could be problematic in recycling rinse water.

Typical treated wastewater is:

- Very low in dissolved metals to meet treatment regulations
- High in total dissolved solids (TDS) from neutralization and treatment
- Consistent pH, typically slightly alkaline from metal precipitation process
- At room temperature
- May have some other residuals such as soaps, surfactants, or emulsifiers

The reuse of water will also depend on its intended reuse location. If the water is intended for non-critical rinses, then the final water quality will not be as critical as for use in topping off a plating tank or other use requiring high purity. The water quality criteria needs to be considered early on to determine what treatments are required to obtain the proper water cleanliness for reuse.

Both chemicals and labor were used to treat this wastewater and money was spent to purchase the water and send it to the sewer, so reusing the water in the process is a means of recovering a portion of that cost. A reverse osmosis (RO) system is one means of recovering at least 50% of this treated water and making it very useable as rinse water again.

TDS removal with RO system

The most effective means of removing TDS is reverse osmosis (RO). The process is ideal for removing dissolved materials from water and has become a vast technology for desalinization and potable water purification. System efficiency (water yield) is based on multiple factors including reverse osmosis membrane type, and equipment design such as pressure limits, membrane area, number of cycles, etc.

Reverse osmosis is a technology that filters water with a membrane and allows only water molecules and small amounts of sodium, chloride, or potassium to pass through the membrane (0.5 to 3% leakage of salts is typical). The actual process works by applying pressure to the “dirty” water which forces the clean water through the membrane and leaves the larger molecules and ions behind. Figures 1 and 2 show simple schematics of the RO process and how it works.

Figure 1
Simple explanation of osmosis and reverse osmosis

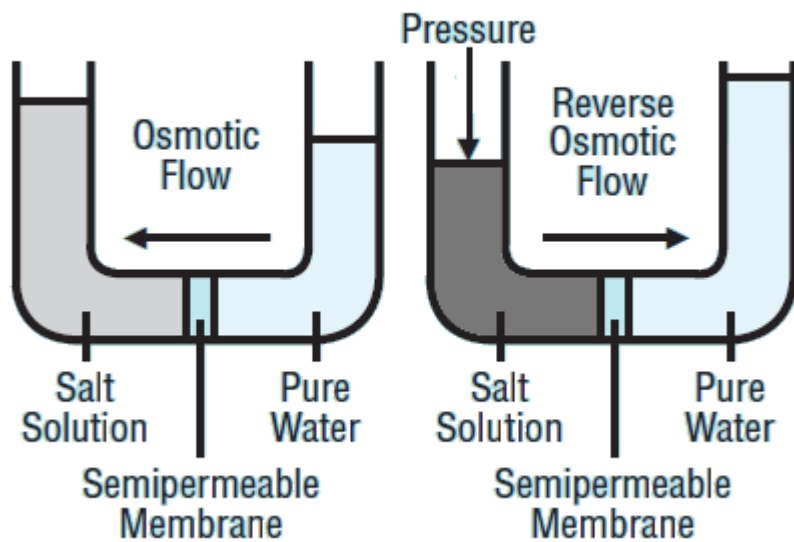
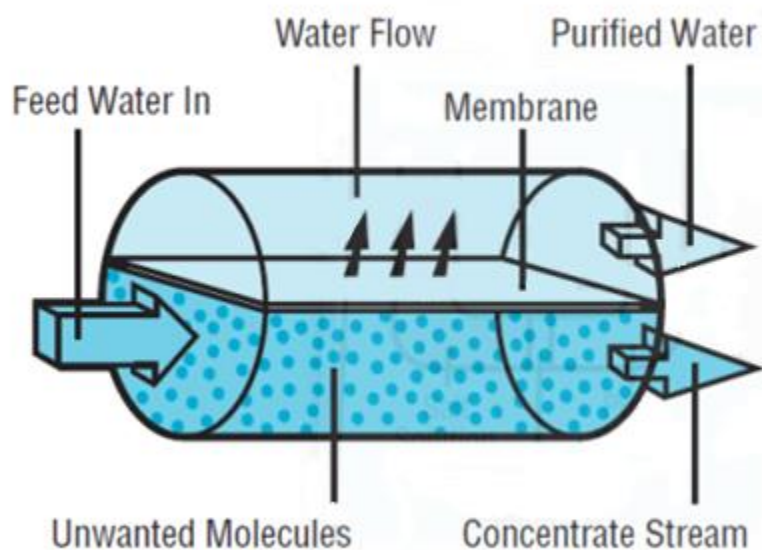


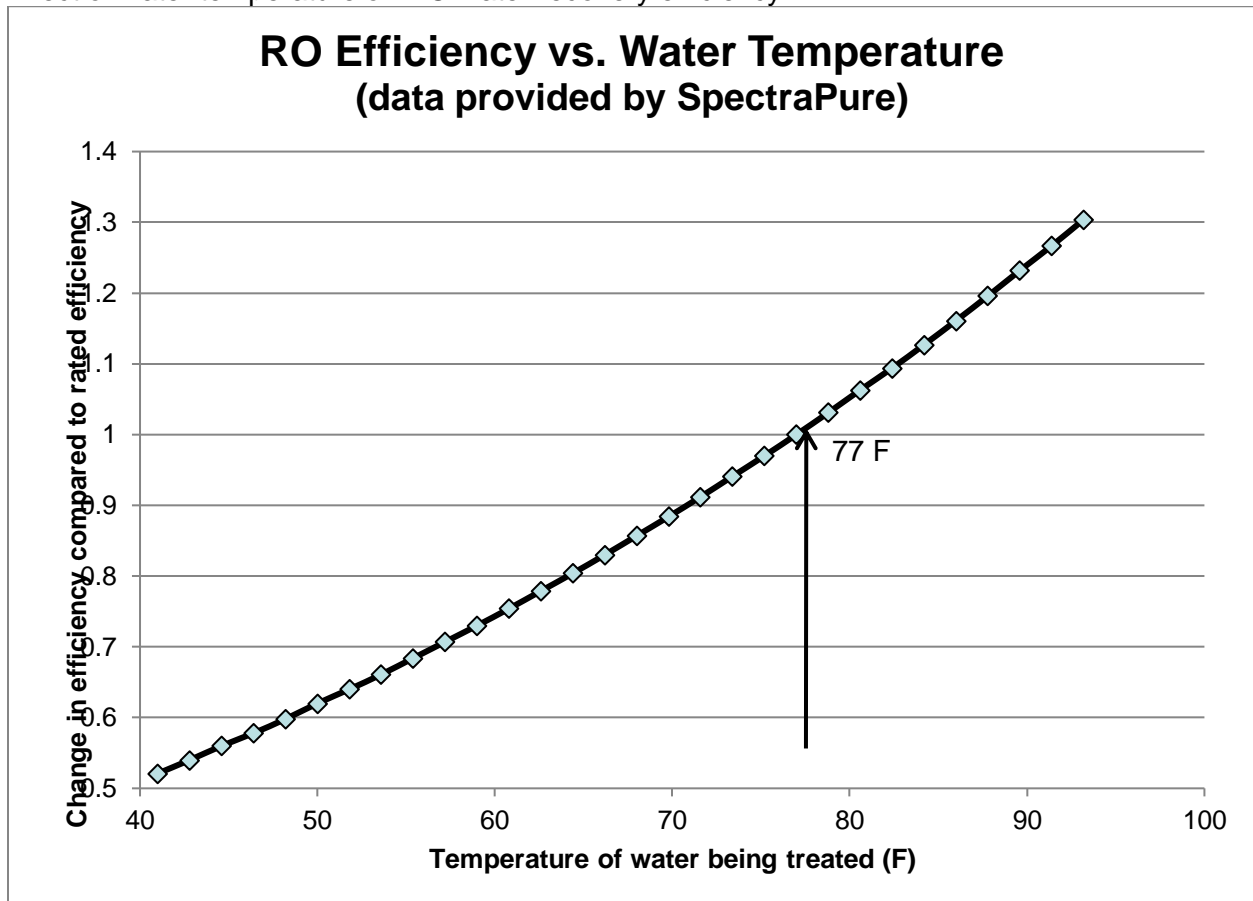
Figure 2
Schematic of how an industrial RO system would work with input water and two output streams





The incoming water properties have an effect on RO recovery efficiency. The incoming TDS levels have a large impact on pure water yields. Higher TDS levels result in lower pure water yields and vice versa. Cold water has much lower yields than warm water. Figure 3 is a typical recovery curve for an RO system at various incoming water temperatures.

Figure 3
Effect of water temperature on RO water recovery efficiency





The RO membrane type will determine the pH limits, temperature limits, membrane life, and potential water pretreatment requirements such as chlorine removal. Table 1 shows the three most common RO membrane categories and their characteristics.

Table 1

Typical RO membrane types and characteristics

| | | | | | |
|---|--------------------|--------------------------|-----------------------|-------------------------|---|
| Cellulose Acetate | Low cost | Medium water flow | pH range 4-8 | Max. temp. 95 F | Oxidation resistant |
| Composite (thin film composite, TFC) | High cost | High water flow | pH range 2-11, | Max. temp. 113 F | Vulnerable to oxidizers (chlorine) |
| Aromatic Polyamide | Medium cost | Low water flow | pH range 4-11 | Max. temp, 95 F | Oxidation resistant |

Advantages of RO filtration:

- Removes everything: ions*, bacteria, viruses, solids, dissolved solids
- Relatively simple, low maintenance system

Disadvantages of RO Filtration:

- Low temperature water produces lower pure water yields
- Higher TDS water produces lower pure water yields
- Tends to leak small amounts of single charge ions (Na⁺, K⁺, Cl⁻)
- Membrane can foul rapidly if suspended solids are high (may require pre-filtration with an ultrafilter)
- The RO process is relatively slow such that the most economical RO unit will be running during both production and non-production hours (filtering stored treated wastewater and storing filtered water during off hours)
- May require pre-treatment to remove chlorination chemicals

Current technologies allow up to about 80% fresh water yields. More typical yields are 50% at optimum conditions of temperature and minimal TDS levels. Even with recovery rates of 50% typical RO systems have a payback of one to two years with water cost. As an example from a case study, an RO unit rated for 15,000 gallons per day water recovery would cost approximately \$20,000 and save approximately 3.2 million gallons per year (\$17,000 savings/year).

Before purchasing an RO system it is important to implement other water savings measures first so that the RO system is properly sized for the reduced water volumes. Otherwise, the RO system will be underutilized as other water savings measures are implemented.

Example of a small industrial RO system



RO Ultratec 20,000 GPD System

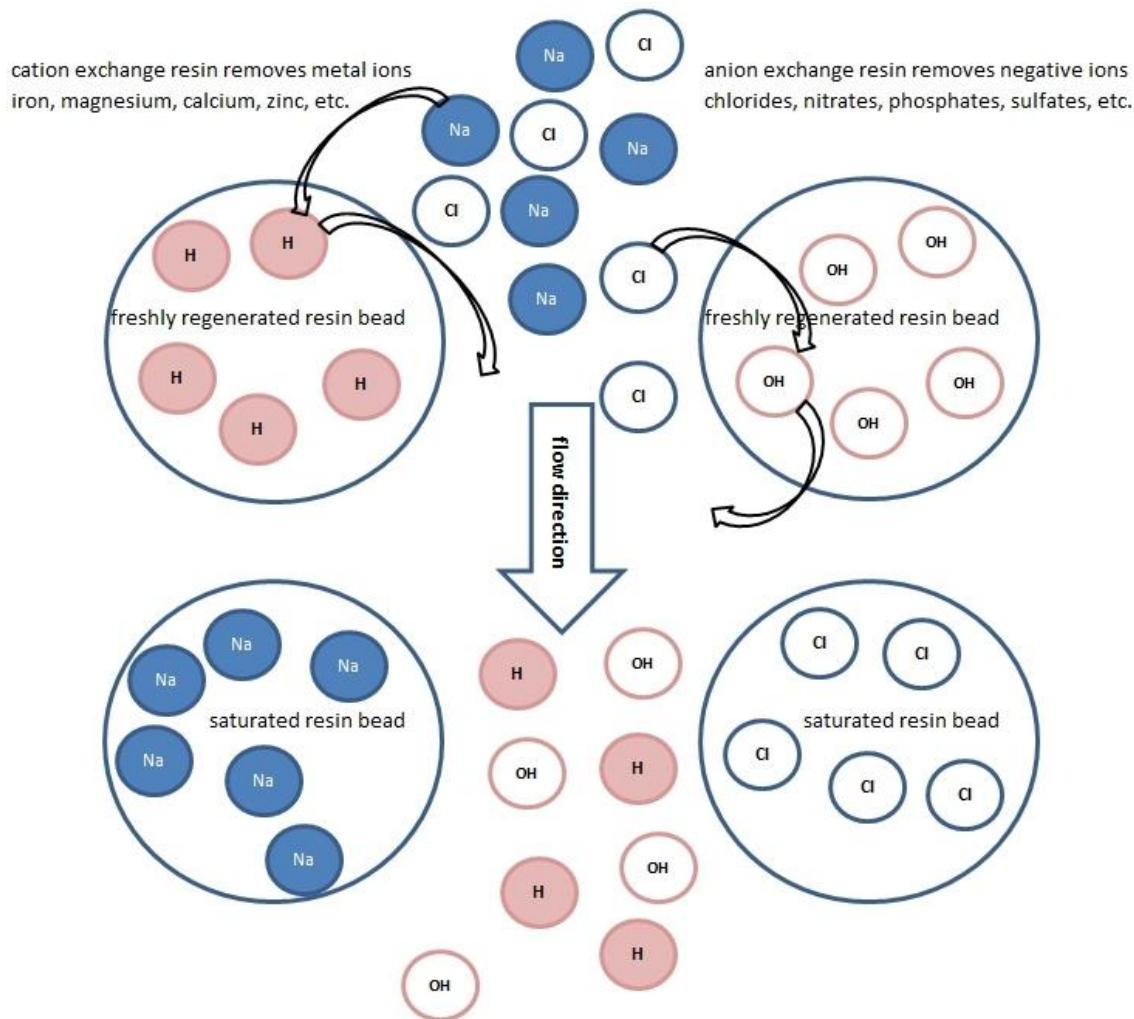
Water Deionization

For critical water purity, treated wastewater can go through both an RO system followed by a water deionization system (ion exchange resin column system). The RO system will remove the majority of the ions, suspended solids, bacteria, dissolved organics, etc. but will leave small residuals of sodium, chlorides, and potassium ions. If these ions need to be removed for critical rinsing or chemical tank makeup water then the next step would be deionization (DI).

Figure 4 shows the mechanism of deionization for both positive and negative ion removal. Following deionization the water will be of high enough purity to allow both critical rinsing and chemical tank makeup water. Only in the most extreme conditions would additional treatment be required, such as carbon dioxide removal, to obtain ultra-pure water.

The DI system should be sized for water demand and expected ion loading rates. An ion exchange resin can take only a certain amount of ions per cubic foot before the resin must be regenerated to flush out the adsorbed ions. After regeneration the resin is able to be reused. The waste chemical used in flushing out the resin will need to go to waste treatment due to either high acidity or high alkalinity. If resin columns are too small for the water volume and ion loads, the regenerations will have to be done too frequently. An oversized system will be regenerated much less frequently but runs the risk of developing biological growth inside the column. Hence the importance of properly sized systems.

Figure 4
Explanation of how deionization resin beads work





Ventilation Efficiency in Metal Finishing

Overview

There are ventilation costs associated with both plating and painting lines, both associated with removing hazardous materials from the air. A plating line can have a large ventilation system to vent either a large number of process tanks or to ventilate individual large tanks. A paint line using high VOC paint will have a special ventilation system to handle the flammables in the paint fumes during the spraying operation as well as ventilation during the drying operation.

In the northern US, any air vented out in the heating months requires the heating of incoming, cold outside air. So reducing the total air exhaust has an immediate energy savings due to heating cost reductions.

The larger the exhaust system, the greater the cost to run the ventilation system. The following table shows the increase in both the air heating and electricity costs as a ventilation system increases in size.

| Exhaust CFM | Blower hp | Annual electricity cost, \$.09/kW-hr | Annual make-up air heating cost, \$5/decatherm of natural gas | Total annual ventilation, heating cost |
|-------------|-----------|--------------------------------------|---|--|
| 10,000 | 50 | \$23,696 | \$6,463 | \$30,159 |
| 8,000 | 40 | \$18,957 | \$5,170 | \$24,127 |
| 5,000 | 20 | \$9,479 | \$3,231 | \$12,710 |
| 2,000 | 10 | \$4,739 | \$1,293 | \$6,032 |

Methods of reducing ventilation

Plating lines:

- Variable frequency drive fan motor that can run the ventilation flow at lower rates after process tanks have either been covered or cooled.
- Automatic tank covers linked to variable flow rate exhaust system. The exhaust flow can increase or decrease depending on the number of tanks with the lids open
- Push-pull tank vents that increase the air velocity across the surface of the tank, therefore reducing the total air flow needed to capture fumes.



Paint lines:

- If the line consists of independent booths or workstations then the ventilator to each work station can be tied into its spray system. After the spray system is turned off, the ventilation fan can shut down after a time-out period. Therefore, the ventilation will be directly tied to production.
- Booths should be sized for the work. If the largest parts or part array is two feet by two feet then the booth ventilation area should be proportioned to that area. There is no need to ventilation this example with an eight foot by eight foot ventilation area.
- If the ventilation system is one large system for multiple booths then the ventilation fan could have a variable frequency drive motor tied in with damper controls on each booth. When a booth is not active, the damper will close and the ventilation rate will drop accordingly.



Alkaline Cleaning

Overview of Alkaline Cleaning

In the typical metal finishing process, the alkaline cleaning tanks are first in line and take the bulk of the dirt load. Whether the tanks are soak cleaners, ultrasonic assisted cleaners, or electrocleaners, their purpose is to remove oils, grease, wax, polishing compound, particulates, and light oxides from the part surfaces. Depending on the detergent additives in these tanks, the tanks could build up surface oil, oil emulsions, suspended solids, or sludge at the bottom of the tank or any combination of these contaminants. As with acids, the cleaning chemicals are consumed in the process of removing and preventing redeposition of the contaminants.

Bath chemistry control

First, there should be a procedure in place to monitor the alkaline cleaning strength of a bath. It may be as simple as measuring the pH or as complicated as sending a sample out for chemical analysis. Typically the cleaning chemistry supplier can either do the testing or provide test kits or test methods to monitor and correct the cleaning chemistry as it ages.

Surface oils

The surface oils can be segregated and removed by a combination of surface sparging to a weir and the use of various oil skimmers available on the market to pull the accumulating oil from the weir. What needs to be avoided is “dead zones” on the tank surface where oils can accumulate and be redeposited as parts leave the tank. A well designed sparger will push a uniform layer of surface water across the tank and over the weir. This surface layer will contain a film of oil that can then be concentrated in the weir trough where it can be skimmed by various methods (belt skimmer, disk skimmer, concentrator vanes).

Example of the sparger and weir system in a Grease Monkey Classic, manufactured by Blackstone Ney



Note that normally the water level would be higher such that the sparger tube would be half submerged and water would be flowing over the weir. For photo clarity, the tank level was lowered to show the water jets from the sparger. If the system was actually operated this way there would be a chance of foaming.

Particulate

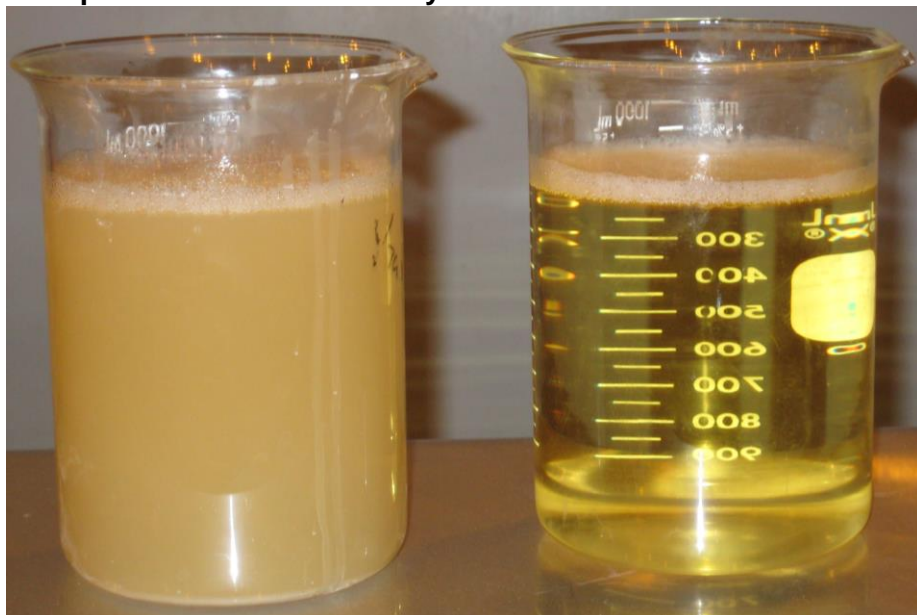
Third, the heavy particles that can settle on the bottom of the tank can be removed by bag filtration or some other simple filtration method. Removal of the heavy solids is especially important if the cleaning tank has ultrasonic transducers on the bottom of the tank. A layer of dirt covering the ultrasonic transducers will reduce the efficiency of the ultrasonic cleaning action. The filtration system needs to be sized for both the expected particulate size and particulate loading. Heavily soiled parts may require a dual filter system that can be switched as alternate side gets loaded allowing filter change-outs on the fly.

Emulsions and suspended solids

Finally, there are the emulsified oils and suspended solids. These are more difficult to remove by normal filtration methods. **Ultrafiltration** is a method that can often break the oil emulsions and remove the suspended solids without removing the active cleaning chemistry. The ultrafiltration type will depend on the pH of the cleaning chemistry and the bath temperature. Polymer filter types are quite capable of removing suspended solids and emulsified oils but cannot tolerate elevated temperatures or extremes of pH. Some of the commercially available polymer ultrafiltration systems can handle pH from 0 to 14 and temperatures up to 158°F (Koch Membrane Systems, SelRO®). One ultrafiltration system manufactured by Arbortech Corporation

has filtration capability of a 1 to 14 pH range and temperature limits of over 200°F. Therefore, this system can easily filter hot alkaline cleaners without filter damage. For whatever ultrafiltration method used, the resulting filtered cleaning solution should provide minimal loss of the cleaning chemistry and maximum removal of the suspended solids and emulsified oils such that the cleaning chemistry is ready to use again.

Example of a cleaner filtered by an Arbortech filtration unit



The prefiltered sample is on the left; the filtered sample is on the right.

Centrifugation

Another method that may produce good results is **centrifugation** of the cleaning solution. There are many continuous centrifugation systems that will provide oil-water separation, water-solids separation, or both. The effectiveness of this method for oil emulsion removal will depend on the strength of the emulsion created by the cleaning chemistry. Some chemical emulsifiers are so strong that a typical centrifuge cannot break the emulsion.

Centrifugation can typically handle suspended solids (colloidal particles) but will still depend on particle size and centrifugal forces. Bench testing may still be necessary to confirm the process feasibility.



Rinsing

Rinse Water Options

It may not be typical for all metal finishing operations but it is fairly common to have water costs at or near the top of the cost of operations. Rinsing is critical in the metal finishing process but more water use does not necessarily mean better rinsing.

Best practices for producing effective rinsing are:

- Double counterflow immersion rinse tanks between process tanks
- Reactive rinsing for the appropriate process chemistry combinations
- Spray rinsing
- Rinse controls such as automatic valves controlled by timers or water conductivity limits

Immersion rinse efficiency model

Often times, when the rinse appears to be inadequate, companies assume that the best method of improving an immersion rinse is to increase the flow rate. However, rinse flow rates can be deceptive in that high flow rates may not be as helpful as expected. Figure 1 displays a single rinse tank with chemical dilution over time at various flow rates. The initial conditions are:

- 100 gallon rinse tank
- Incoming (dragout) solution concentration of 100 grams/gallon
- Dragout volume per rack of 0.05 gallons

It is apparent from Figure 1 that the rinse tank does not dilute the dragged in chemical very rapidly. Even the 25 gpm flow rate takes approximately 5 minutes to drop the concentration from 5% to 2.5%. The main point is that a single rinse tank is relatively ineffective at providing critical rinsing. More importantly, increasing the flow rate in a rinse tank does not necessarily improve rinsing unless extremely high and costly flow rates are used.

By taking immersion rinse flow rates one step further, Figure 2 shows the same rinsing example as shown in Figure 1 with the exception that every 10 minutes an additional load of dragout chemical is added. Note that this causes the rinse tank concentration to rise to very high concentrations very quickly regardless of the flow rates used. This is the primary reason that counterflow rinsing is so effective. The concentration of the dragout chemistry between the first rinse tank and the second rinse tank drops dramatically in a double rinse setup. Thus the effective contaminant dilution rate is much faster as shown in Figure 3. For this model, the dilution between the first rinse tank and second rinse tank is a factor of 100.

Figure 1
Rinse water flow dilution rates

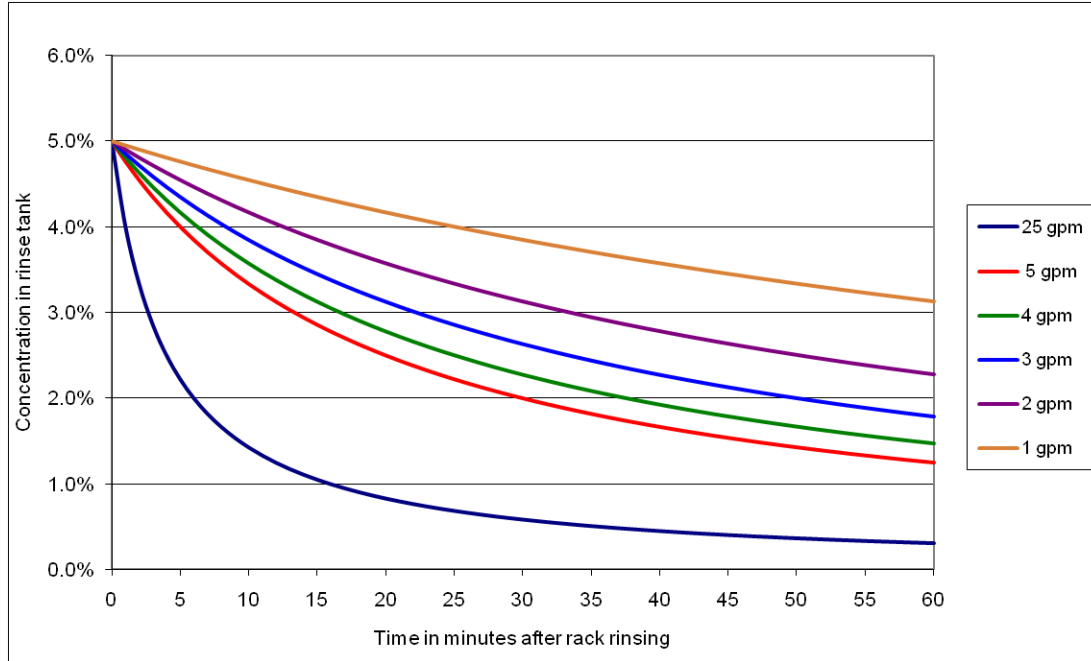


Figure 2
Parts rinsed in tank every 10 minutes vs. single rinse

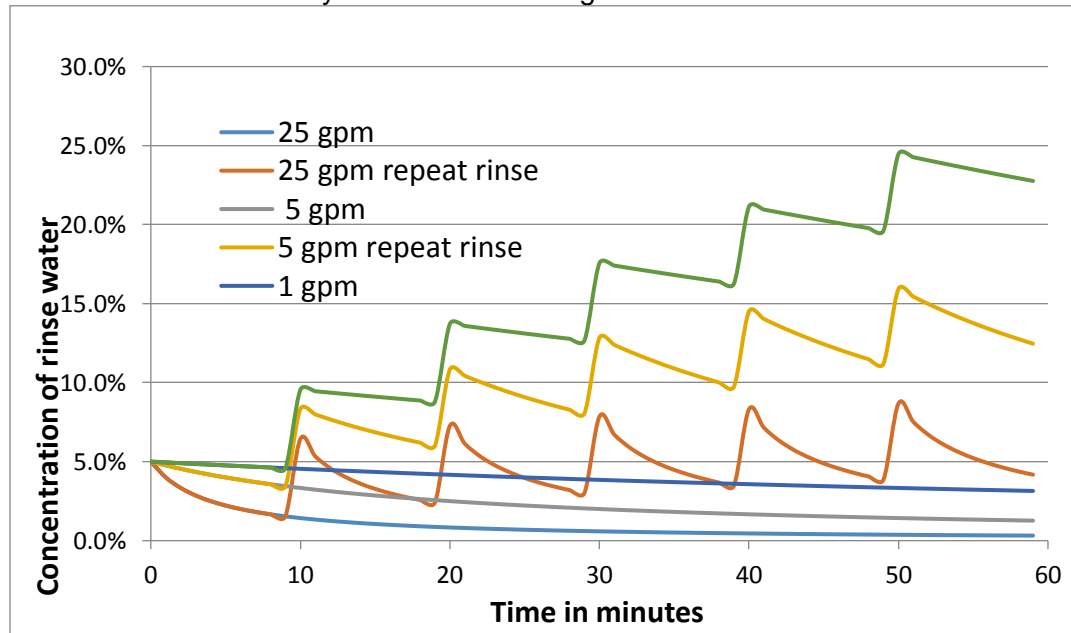
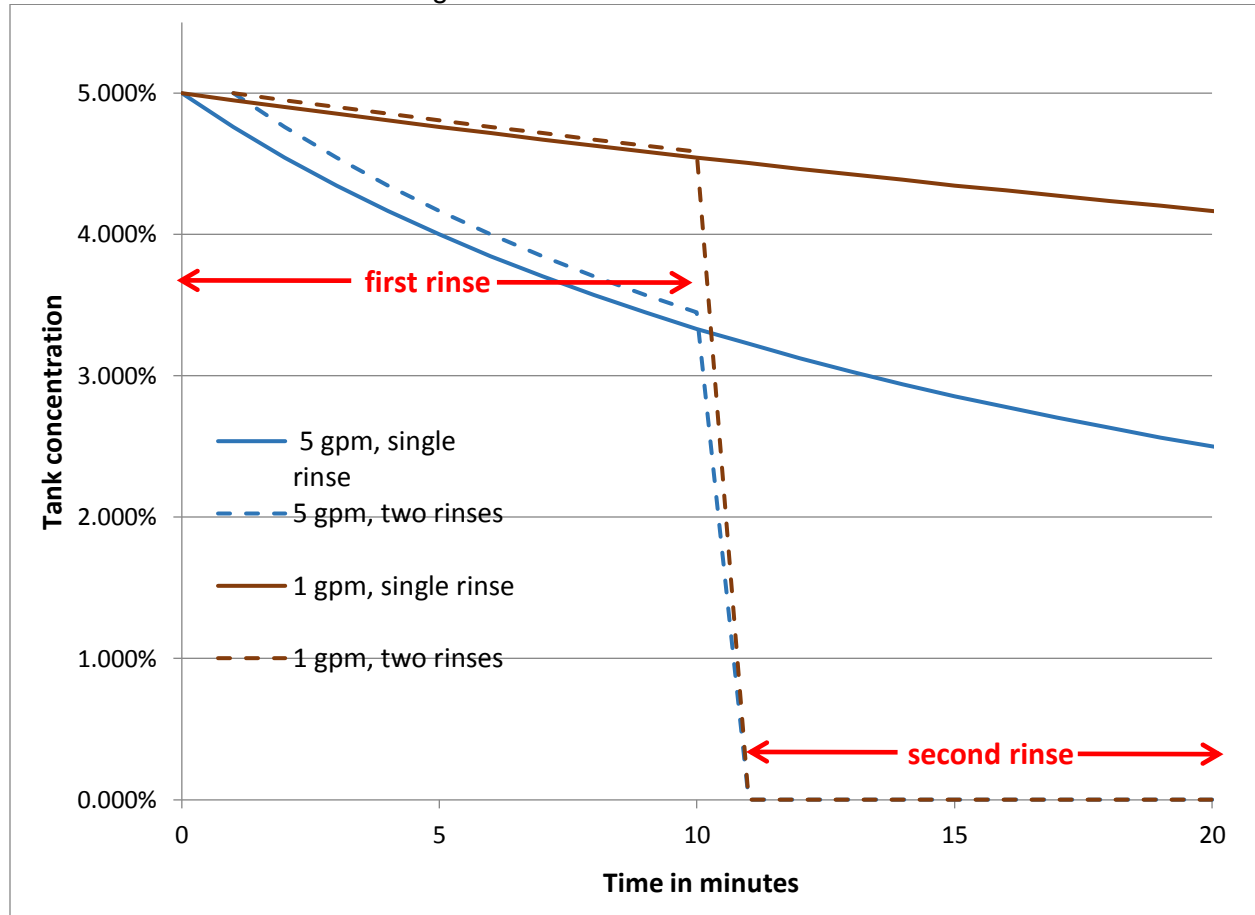


Figure 3
Contaminant concentration in single rinse tank and two-tank counterflow rinse.

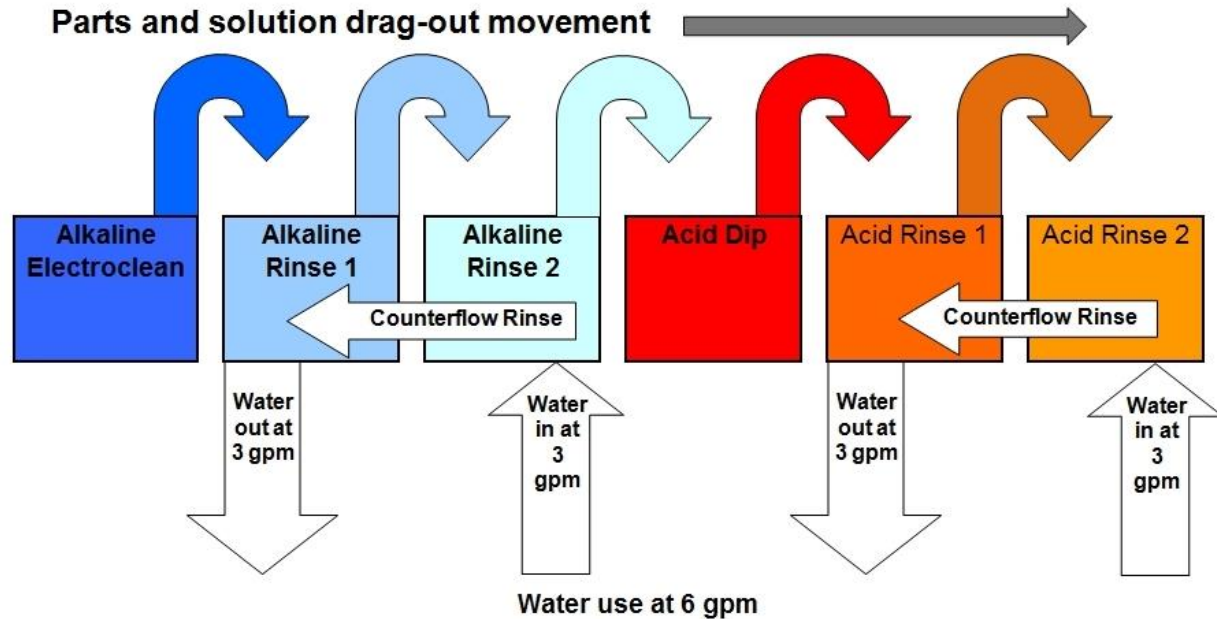


Counterflow (countercurrent) rinsing

There are two means of reducing the water use in rinsing without reducing the rinse effectiveness. The first is called counterflow or countercurrent rinsing where the relatively clean rinse water from the second rinse in a rinse tank pair is flowed to the more contaminated primary rinse tank. Therefore cleaner water is always moving to less clean rinse tanks. The cleanest water is still used for the critical final rinse but the same rinse water is reused for the initial and least critical rinse. Figure 4 shows typical two-tank counterflow rinse systems, one for acid rinsing and one for alkaline cleaner rinsing.

Figure 4

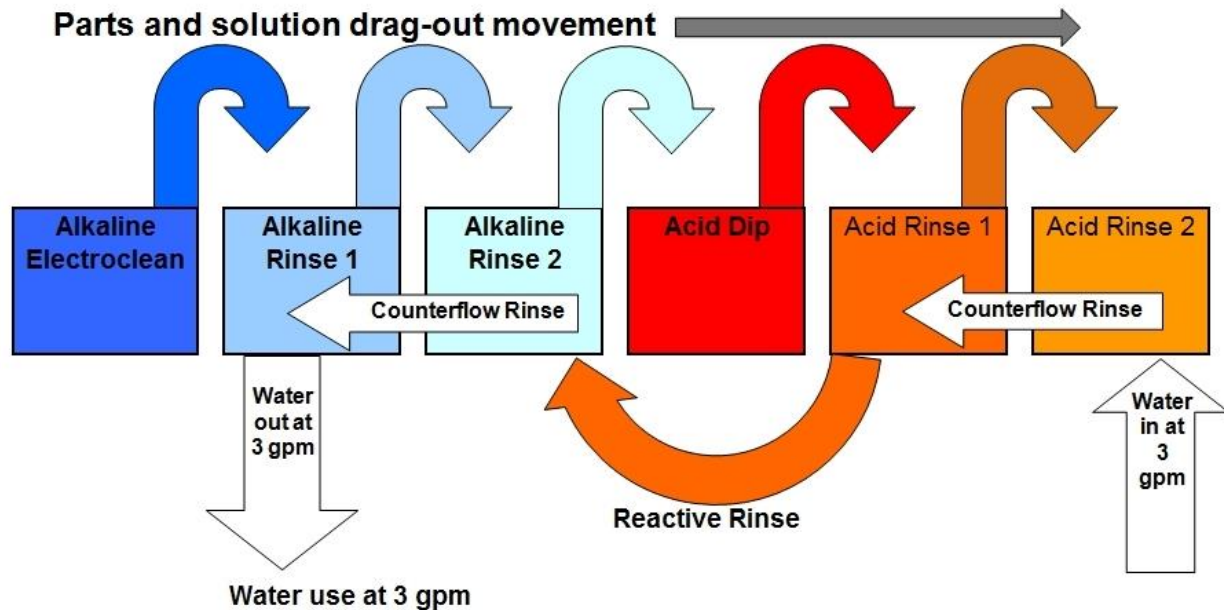
Two sets of counterflow rinses, one after alkaline cleaning, one after acid etch



Reactive Rinsing

The second less commonly used method of reducing water use is called reactive rinsing. It is a method of taking rinse water around a process tank to a previous rinse tank. The example in Figure 5 shows acid rinse water (acid rinse 1) flowing to the last alkaline rinse tank (alkaline rinse 2). The acid contained in this rinse water would normally be sent to waste treatment. With reactive rinsing, the acid from acid rinse 1 now goes to alkaline rinse 2 and neutralizes the residual alkalinity in that water. Any rinse water from alkaline rinse 2 being dragged out by parts and racks to the acid tank will now contain acid which previously would have been wasted. Therefore, no acid is being neutralized by alkaline dragout to the acid tank and acid previously lost in acid rinse 1 now is partially recovered by the reactive rinse flow.

Figure 5
Maximized use of counterflow and reactive rinsing

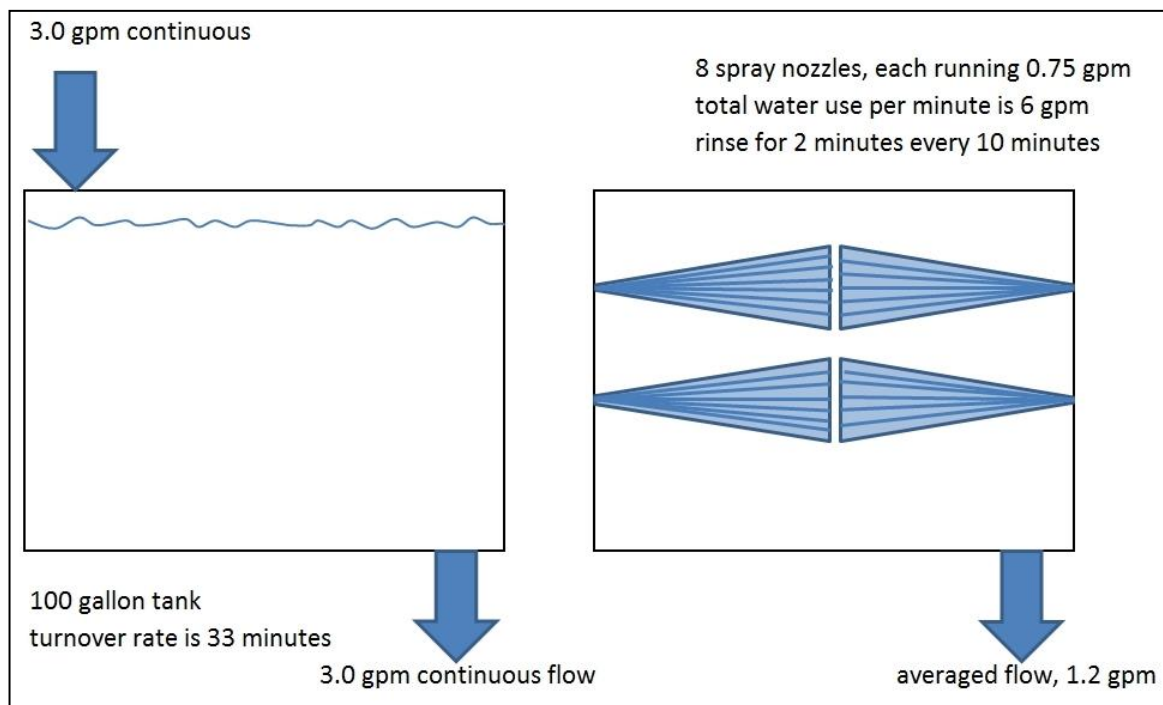


Spray rinsing

The final method of reducing rinse water volumes but still obtaining excellent rinsing is by spray rinsing. This method is somewhat limited by the geometry of the parts being rinsed in that complex geometric shapes are difficult to thoroughly rinse with an automatic spray system. In a manual line, the operator can overcome the geometry problem of a part by manually spraying the part areas which are difficult to rinse by a normal battery of spray nozzles. Figure 6 compares a spray rinse to an immersion rinse. There are two major advantages to spray rinsing over immersion rinsing. First, the water hitting the parts is always clean unlike water in an immersion tank which always contains some residual contamination. Second, a spray rinse needs to be running water only when parts are being rinsed. The rest of the time there is no water use, which is both a cost and environmental savings. A third and lesser advantage to spray rinsing would be in the case of parts requiring a heated rinse. In-line demand heaters can be used to provide hot water as needed during the spray cycle rather than having to continuously heat an immersion rinse tank.

The spray system in Figure 6 illustrates the water savings associated with spray rinsing compared to immersion rinsing. The left illustration in Figure 6 is a typical immersion rinse tank running at 3 gpm. The right illustration is a spray rinse with a battery of 8 spray nozzles with a combined spray volume of 6 gpm. The spray rinse in this scenario is only turned on for two minutes while parts are in the tank. The next set of parts arrives eight minutes later. Since the spray rinse is turned on only for 2 minutes out of a 10 minute period, the average water use is 1.2 gpm which is less than half of the immersion rinse tank's usage rate of 3 gpm.

Figure 6
Spray rinsing compared to immersion rinsing



Rinse flow controlled by flow restrictors

One final way to reduce rinse water use in immersion rinse tanks is by controlling the rinse water valves. This method is a means of limiting flow when rinse water control consists of manually operated valves. The simplest method is to insert flow restrictors on the water valves to limit the maximum flow regardless of how open the valve is.

Rinse flow controlled by rinse water conductivity

Another method of water valve control is to insert solenoid valves into the rinse water lines which open or close based on the conductivity of the rinse water in the tanks. This requires minor up front measurements of the water conductivity which is often directly related to the amount of chemistry being dragged into the rinse water. The valve conductivity controls are then set to turn the water on when the conductivity (contamination) gets too high and then turn the water off when the conductivity drops to a lower set point. The advantage of this system is that the water stops running when a plating line has a break in the work flow, rather than manually turning the water on and off at both the beginning and end of the day regardless of the amount of work running through the line. These conductivity controlled valves can be purchased as systems which include the solenoid valve, conductivity probe, and conductivity control box, and typically cost between \$500 and \$1000.



Rinse flow controlled by timer

A third method is to use a timed rinse. A timer controls a solenoid valve to open and close water flow to the rinse tank. The operator turns on the rinse timer when placing the parts in the rinse tank and the rinse water turns off after a preset time. In this way the water is running only when parts are in the rinse tank and is very useful for irregular process cycles or for processes where there are frequent periods with no parts going through the line.

Rinse Water Options

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Best practices for producing effective rinsing are:

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By taking immersion rinse flow rates one step further, Figure 2 shows the same rinsing example as shown in Figure 1 with the exception that every 10 minutes an additional load of dragout chemical is added. Note that this causes the rinse tank concentration to rise to very high concentrations very quickly regardless of the flow rates used. This is the primary reason that counterflow rinsing is so effective. The concentration of the dragout chemistry between the first rinse tank and the second rinse tank drops dramatically in a double rinse setup. Thus the effective contaminant dilution rate is much faster as shown in Figure 3. For this model, the dilution between the first rinse tank and second rinse tank is a factor of 100.



Acid Etching and Acid Cleaners

The starting point for extending the life of an acid bath is having good process controls for the acid bath. Without good monitoring and acid addition methodology, an acid bath can be prematurely disposed of just because the acid strength was not kept at the proper level. If an acid tank is minimally managed, such as running a tank for a month and then disposing of it with no acid additions or titrations over that time period, then the tank effectiveness is variable and unknown over the life of the bath. This could lead to plating or finishing defects as the tank chemistry ages. If the acid was in reality in good condition at the time of disposal, then disposing of the tank is a needless waste of acid and an added cost to treat the acid waste. In a direct assistance project, the New York State Pollution Prevention Institute was able to reduce a 500 ton per year acid waste stream to a 250 ton per year waste stream at a savings of almost \$200,000 per year. Rigorous acid management practices were used to produce these savings.

Good process control means that there is a routine chemical analysis of each acid tank. On a weekly basis, and in the case of high production lines, a daily titration of the acid baths may be necessary to properly control the acid strength. Then there should be equally regular acid additions to the acid tanks based on the titration results to bring the acid levels back to their original strengths. For large operations there are systems available that can do the titrations and acid additions automatically, such as Scanacon titration and acid dosing equipment.

Second, and usually less frequently, each acid tank should be measured for dissolved metal content. These two tests, titration and metal analysis, are the basic requirements for the proper function of the acid tank chemistry.

The main reason to dispose of an acid tank and start with a fresh chemistry is due to dissolved metal concentrations being high enough to interfere with the acid-metal reaction. Therefore, a means of extending the bath life involves either removing the dissolved metal or converting the dissolved metal to a form that no longer interferes with the acid-metal reaction.

Commercially available methods dealing with the dissolved metal problem¹

1. Additives to precipitate and/or sequester the dissolved metal
2. Diffusion dialysis
3. Acid sorption

¹ Note that each of these technologies work best with dissolved metals that form a positive ion in solution (Fe^{+3} , etc.). Metals that form a negative ion complex (TiF_6^{-3}) are very difficult to remove with a reasonable efficiency in any of the methods discussed.

Additives

Metal precipitation/sequestering is an in-tank means of removing a portion of dissolved metal by precipitation and a portion by sequestering the dissolved metal into some sort of soluble complex that no longer competes with the acid reaction. PRO-pHx™ (www.pro-phx.com) is one example of such a chemical method. PRO-pHx has a proprietary formulation which acts to form fine precipitates in the acid tank which gradually get filtered out in a filtration system.

In normal operating use, PRO-pHx is added to the acid tank to maintain a 1% concentration of the additive. A portion of the dissolved metal forms a precipitate that can be filtered.

Example of a filter with a thick layer of metal precipitate using PRO-pHx

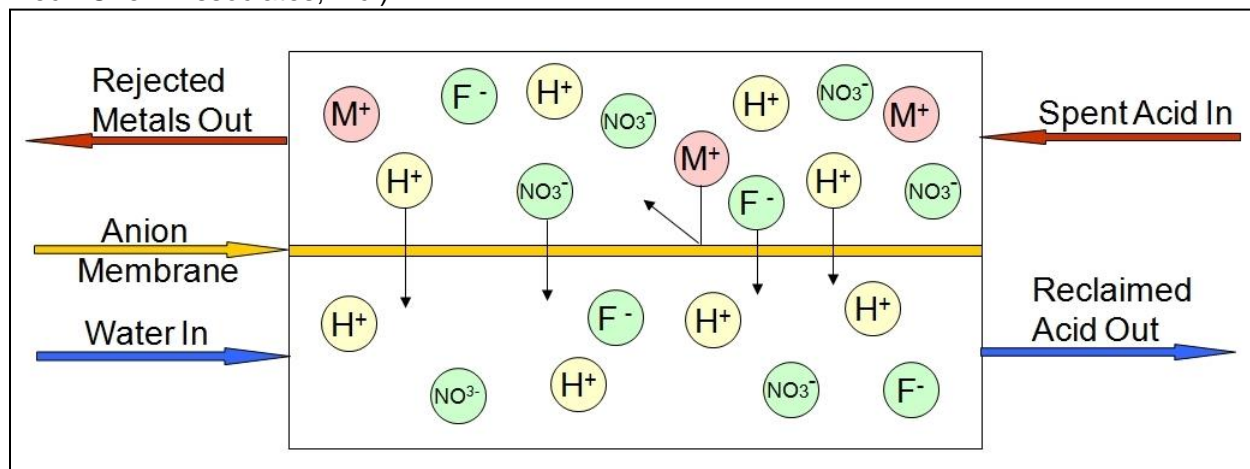


Diffusion dialysis

The diffusion dialysis process makes use of a membrane that allows the acid's negative ions (SO_4^{2-} , NO_3^{2-} , Cl^{-1} , etc.) to pass through while preventing the positive metal ions ($\text{Fe}^{+?}$, $\text{Al}^{+?}$, etc.) from passing through. A typical system is up to 90% efficient, meaning that 90% of the acid is recovered and 90% of the metal is removed in each membrane pass. The results are a waste stream which is high in dissolved metal and an acid stream that can be returned to the acid tank. Routine use of diffusion dialysis on an acid tank results in a stable, low level of dissolved metal in the acid tank. As with any acid tank, there is still the need to add fresh acid since acid is still being consumed in the process of dissolving metal. One company that produces small to large diffusion dialysis equipment is Mech-Chem Associates, Inc.

Figure 1

Diagram showing the process by which diffusion dialysis recovers acid (diagram provided by Mech-Chem Associates, Inc.)



Acid sorption

The process of acid sorption works on a similar principle to ion exchange in a water deionization system. The acid anions (negative charge) are captured from the acid solution stream by an ion exchange resin while allowing the positive metal ions to pass through. Then the resin column is back-flushed with fresh water to free the acid anions. This back-flushed solution is therefore rich in acid and poor in dissolved metal. The acid rich solution can then be returned to the acid tank. This method is between 80 and 90% efficient depending on the metal ion and acid anion charges.



Part Drying

It is important to define the goal or goals in the process of drying parts after the finishing operation. Is it to prevent rusting before some additional steps, to avoid water spots resulting in some cosmetic problems, or is it to provide dry parts for the next operation?

Water spotting

The easiest way to prevent water spotting is with the use of DI (deionized) water in the final rinse. The water spots are typically due to minerals in normal process water and can be eliminated by removal of the minerals.

A second method that at least will minimize water spots is with an air blow-off process to remove the water droplets before they have time to dry on the parts. This method will be very dependent on part geometry and part orientation on the racks. If the air cannot reach certain areas on the parts due to geometry or if parts block each other then the spotting may still occur in those areas.

The Drying Process

Ideally the method or methods employed to dry parts should be as energy conservative as possible. For example, high pressure blowers should be used instead of compressed air since the electricity costs are much lower for blowers than compressors. As a side note, the risk of getting air carried contaminants on the parts is higher for compressed air than with blowers.

Hot final rinse

One of the easiest methods of drying parts is with a hot final rinse using DI water. The parts will flash dry if the part geometry does not have any areas allowing water to puddle. This method requires energy to heat the water but totally eliminates the need for any hot air drying.

Air drying

There are two means of drying parts with air, which can be used in conjunction with each other or independently.

- **High velocity air**
Primary purpose is to knock the water off the parts rather than dry the water off the parts. One manufacturer of high velocity drying systems is Sonic Air Systems.
- **Heated air (convection drying)**
Primary purpose is to evaporate the water off the parts. These means that the parts have to warm up in the heated air to effectively evaporate the water

- **Combination; hot and high velocity air**
This combination allows the parts to dry rapidly without the necessity of heating the parts up to cause evaporation. The large water droplets are knocked off the parts and any residual fine droplets are evaporated.

Example of an air knife drying system with blower



Image courtesy of [Sonic Air Systems](#).

Infrared drying

Infrared (IR) is a line-of-sight method of drying parts that is energy efficient compared to convection heating of parts. The IR light is rapidly absorbed by the surface of the part resulting in a high surface temperature. Water remaining on the part surface is rapidly evaporated without the need for the whole part to reach a high enough temperature to cause evaporation. Since the process is line-of-sight, it is best used for either thin parts that allows rapid through-heating of the part and part cavities, or best used on flat parts such as panels which have simple geometries.

Example of typical quartz tube IR panel with ceramic fiber reflectors





Phosphating

Overview of Phosphating

The process of phosphating aluminum and steel parts is typically listed as a conversion coating because the process involves metal removal as part of the reaction. However, it is not like anodizing or black oxide in that the phosphate coating is actually a precipitation reaction. The final surface is a layer of very fine phosphate crystals adhering to the surface of the metal.

For paint and powder coatings, a phosphate coating has two main functions. First, the coating provides improved paint and powder coating adhesion since the phosphate crystals act as organic coating anchoring sites. Second, the phosphate layer acts as a corrosion barrier should the organic coating get scratched. In rust creep testing, the rust creep is reduced when phosphate is present under the paint layer or powder coat layer compared to no conversion layer under the organic coating.

Phosphate can be used as a stand-alone coating for other purposes such as lubricity in parts forming but the other functions are beyond the scope of this report.

The most common phosphating chemistries are iron phosphate, zinc phosphate, and manganese phosphate. There are also other phosphating chemistries such as Plaforizing™ which are non-traditional in their chemistry and application since they are single step and typically an organo-phosphate that react with both the organic contaminants and the metal surface.

The main thrust in recent years for improving the phosphate process is to reduce the temperature requirements for the phosphate bath. Some chemistries have been developed that work well at room temperature. In general, there has been a trend from high temperatures, 90 F to 200 F, to much lower temperatures, 70 F to 140 F, resulting in energy savings.

Most phosphating lines are single tank (Plaforizing™ from Carpenter Chemicals, Enviroprep from Calvary Industries, and Ferrox Series from Foster Chemicals), three step, or five step processes. The three and five stage processes are:

Three Stage Process:

1. Clean/phosphate
2. Rinse
3. Rinse/seal



Five Stage Process:

1. Clean
2. Rinse
3. Activated rinse
4. Phosphate
5. Rinse

Or

1. Clean
2. Rinse
3. Phosphate
4. Rinse
5. Seal

The single step processes will be more conservative of both water and energy compared to the three and five stage processes. In the case of the Enviroprep by Calvary Industries, the chemistry is phosphate free but still serves as a surface preparation stage for paint and powder coating.

The three and five stage systems can typically be made more water efficient with flow optimization of the rinses, rinse recirculation, and rinse counterflow, and in some cases, reactive rinses. These systems can sometimes be made more energy efficient by switching to lower temperature phosphating chemistries.