

Metal phosphatizing operations

Metal phosphatizing operations are a large industrial source of phosphorus in wastewater. When companies minimize phosphorus discharge from these operations they save by reducing chemical and water use.

Reducing Phosphorus Discharge and Water Use

Minnesota’s waters must be clean and healthy in order to sustain aquatic life and provide recreational use. Although phosphorus is a nutrient for plant growth, excess phosphorus can speed up the aging process of lakes and streams by stimulating algae growth. This creates high biochemical oxygen demand (BOD) as algae decomposes and uses up available oxygen supplies, sometimes threatening the survival of fish and other aquatic organisms.

The Minnesota Pollution Control Agency (MPCA) is establishing effluent phosphorus limits and phosphorus monitoring requirements for municipal wastewater treatment facilities. These facilities are asking their industrial users to reduce phosphorus in discharges to the treatment plant.

Phosphatizing helps prevent corrosion and prepares the metal surface for improved paint adhesion. Less commonly, phosphatizing is used to improve the lubrication, or slipperiness, of part surfaces. The phosphatizing process can vary widely. For larger, low-volume products that do not require a high degree of corrosion resistance or adhesion a one-stage cleaner/phosphatizer, applied with a spray wand, is commonly used. Large, automated seven-stage conveyorized systems are used for high volume component manufacturing and to meet the highest surface property specifications. Three, five and six-stage systems are also common. A typical five-stage

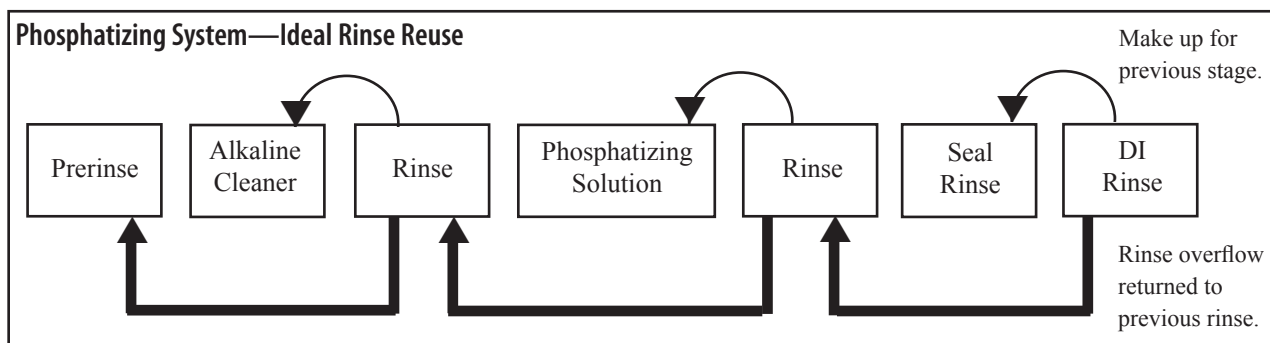
phosphatizing system starts with alkaline cleaning then goes through a rinse, phosphatizing solution, another rinse and finally a seal rinse.

Ideal Rinse Reuse

Many phosphatizing operations were built when water and wastewater disposal costs were low. But, costs have risen and now an ideal system maximizes rinse reuse to minimize chemical and water loss (see diagram below). Overflow from the rinses can be used as make up for evaporation and for dragout losses from the previous static chemical bath, and as a cascade rinse for the previous rinse stage. For a medium-sized five-stage phosphatizing system, a five gallon per minute (gpm) rinse flow—600,000 gallons per year for one shift—is typical. A greater flow rate may indicate an opportunity to decrease water use.

Modify an existing system. The following changes may have the greatest benefits:

1. Reuse water where it will enhance the quality of cleaning. Reuse deionized (DI) water first to maximize the benefit of its purity and because of its cost (see Rochester Powder Coating, page 3). DI effluent from a single stage rinse will generally be cleaner (less dissolved solids) than fresh city water.
2. Cascade the rinses where the overflow volumes are greatest (i.e., greater than five gpm). Cascading the phosphatizing rinse back to the cleaning rinse can cut the rinse flow in half.



And, the acidic phosphate chemical that is returned with the rinse neutralizes the alkaline cleaning carryover that would otherwise degrade the phosphate chemistry. No new contaminants are introduced.

3. Use overflow from the subsequent stage as make up for heated tanks because heated tanks lose the most volume to evaporation.
4. Add a prerinse before the cleaner stage to loosen and remove soils. This keeps a significant amount of soils out of the system, making the cleaning stage more effective. Reuse water by cascading overflow from the cleaning rinse to the prerinse.

Phosphatizing Alternatives

Alternatives to iron phosphatizing have been developed by several conservation coating chemical manufacturers. These alternatives may be based on zirconium, vanadium, or titanium oxides and have been shown to provide corrosion protection and adhesion properties that match or exceed those of iron phosphate coatings. One of the side benefits of these processes is the ability to operate these stages at or near ambient temperatures which greatly reduces energy costs and evaporation.

Water and Chemical Use Reduction Tips

Acid alternatives. Phosphoric acid in the phosphatizing step helps maintain a specific pH. This function can be accomplished by other acids to lower the phosphorus concentration of this stage. Talk to your supplier about these possibilities. If improved paint adhesion to aluminum substrates is the goal, Sol-Gel processes¹ and abrasive blasting procedures² are available.

Bath concentrations. Maintain phosphate bath concentrations and chemical metering of wand applicators within the correct operating range, using the chemical supplier's recommendation. If a range is given, try operating at the low end. This may require greater care by the operators. Lower operating concentrations reduce loading to the rinses, which can lead to reduced flow rates and phosphate losses to effluent.

Reduce carryover. Keep chemistries in their tanks by reducing carryover. Design drain holes in parts where possible and avoid blind holes and recesses. Rack parts for good drainage. Angle them so solutions drain off one point—not an edge—of the part back into the bath.

Design the system with adequate drip time. For dip tank operations, hold parts above the tank to allow the solution to drain back into the tank. Holding parts above the tank for 15 to 30 seconds returns 40 to 50% of the dragout into the tank.

Modify drain boards between stages to drain back to the previous stage. Multistage spray systems should have drain zones between stages that provide for similar drain times—15 to 30 seconds minimum. Consider a fine, low-volume mist arc or spray rinse between stages to remove additional carryover.

Use clean water. Consider using DI or reverse osmosis (RO) water for making up chemical baths and possibly for rinses. DI water greatly decreases the dissolved solids present. This

lengthens bath life and reduces the volume of chemicals used and discharged. It also cuts scaling in heated tanks and the volume of sludge generated by treatment of wastewaters.

Automated systems. Ensure all process controls are properly set (i.e., speed, chemical additions) and that they are periodically calibrated and maintained. Conductivity controls are particularly sensitive—consider using inductive conductivity sensors to reduce maintenance requirements. Quality parts are not an indicator of good system control. Poorly maintained control systems can create quality products by overusing water and chemicals. Frequency of bath turnover may be a better indicator.

Water flow. Measure and control water flow. Flow meters give a quick indicator of water overuse and malfunctions that can lead to overuse. Metering valves can be used with flow meters to control flow rates. In the absence of flow meters, use flow restrictors to control flow. Avoid using ball valves in water lines unless a wide open flow is desired. Small changes in ball valve position can result in large changes in the water flow rate. Although cheap, they are only appropriate as on/off valves.

Filter baths. Filtering remove solids that could build up in the tank or clog nozzles. Skim oil off the alkaline cleaning tank to lengthen the bath life.

Spray nozzles. Clean spray nozzles. Plugged nozzles can cause areas of the parts to be poorly cleaned or coated. A common response to quality failures is to increase the flow and frequency of bath changes when merely cleaning the nozzle could ensure that the solution cleans the parts. Properly position nozzles for an ideal spray pattern to ensure the solution cleans the parts.

Procedures. Train employees on proper operation of the phosphatizing system. Conduct daily inspections to look for tank leaks, valve leaks, evidence of controller malfunctions and plugged nozzles.

Rochester Powder Coating Reducing Phosphorus Discharge

Rochester Powder Coating (RPC) in Rochester is a job shop that paints sheet metal parts using powder coating. Prior to painting, the sheet metal goes through a phosphatizing line. By embracing pollution prevention practices, RPC reduced its phosphorus discharge by 98% over two years.

In October 1995, discharge from the RPC phosphatizing system was 410 milligrams per liter (mg/L) going into the City of Rochester's sewer system. With impending phosphorus limits, RPC and Rochester began to look for ways to reduce this phosphorus discharge. RPC implemented an aggressive approach to maximize the use of phosphate instead of discharging it. First, RPC began to monitor solution content every two hours. This ensured that the concentration was within the proper operating range. They also added more-efficient spray nozzles to the phosphating risers to improve solution contact with parts.

In 1995, RPC installed a five-stage cleaning/phosphatizing system. The system had a partial rinse return to the phosphating bath to prevent loss of phosphorus. Along with installing this system, RPC instituted rigorous monitoring, maintenance and

worker training. In 1997, a sixth stage, DI rinse was added to enhance corrosion resistance and recycle phosphate rinse solution for reuse in the mist rinse just prior to phosphatizing. This provided cleaner parts going into phosphatizing. Although RPC increased production and discharge by 30%, phosphorus discharge concentrations were lowered to eight mg/L.

Federal-Mogul Corporation Identifying Phosphorus Sources

MnTAP funded a student intern at Federal Mogul, Lake City, a manufacturer of diesel and compressor pistons and cylinder sleeves, to identify the sources of phosphorous in its manufacturing plant and to determine a strategy for reducing the quantity ending up in the wastewater. The two main sources of phosphorus were a phosphate coating process (96%) and plant maintenance cleaning chemicals (4%).

During the student's time at the company, all of the cleaning chemicals were switched over to non-phosphorus containing materials. The substitutes performed as well as or better than the conventional phosphorous containing materials.

Changes to the phosphatizing line were suggested. They included typical actions like dragout reduction, fog-like rinsing and counter current flow in tanks. Procedures also were recommended for more routine and careful maintenance of the baths to minimize chemical use and disposal, and to ensure that the proper coating quality was achieved. Approximately 50% of the total phosphorus from the process could be reduced with the above changes.

Hoffman Engineering Company Reducing Water Use

Hoffman Engineering Company, a manufacturer of metal and composite enclosures in Anoka, reduced water use in a painting pretreatment process with the help of a MnTAP intern. Three of the four stages in the pretreatment washer were modified to conserve water. These changes resulted in an estimated savings of \$32,000 and 3.5 million gallons of water annually. Savings from decreased chemical use were not calculated.

Installing flow meters, automated conductivity meters and control valves, Hoffman gained better control of bath concentrations and rinses, which helped identify leaks, malfunctions and decreased the loss of bath chemicals. Drain zones were modified to return more solution to each respective preceding stage.

Treating Phosphorus Discharges

Once phosphorus reduction efforts are put in place, facilities may still need to lower phosphorous concentration in their wastewater. They can be lowered by precipitating phosphorous with ferric chloride, lime or alum. Ferric chloride is generally the most efficient precipitant. The amount of precipitant needed will vary with local water chemistry and the phosphatizing chemicals used. But, adding 20 mg/L of ferric chloride and a 40 minute residence time in the settling tank are reasonable starting points in trying to reach a phosphorous concentration of less than two mg/L.

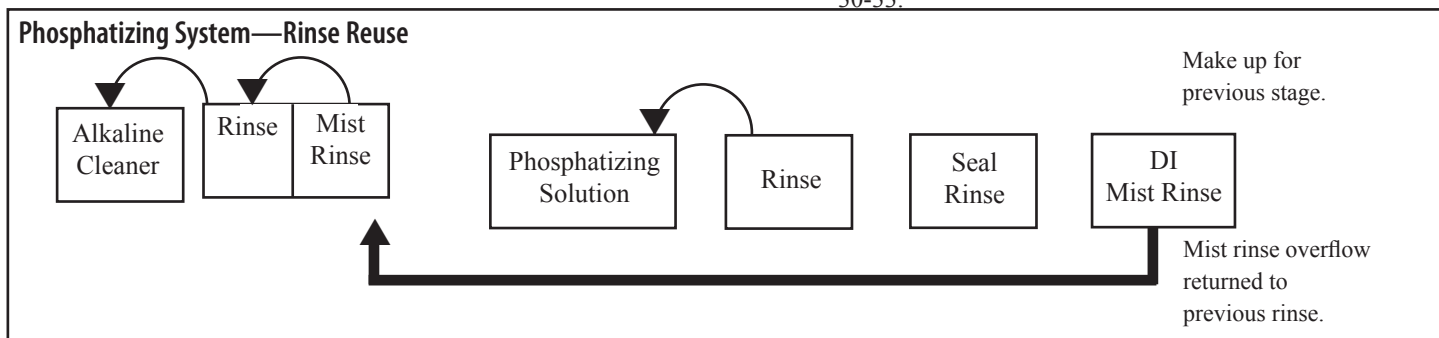
Regulations

Categorical discharge permits. Facilities that perform metal phosphatizing are subject to the U.S. Environmental Protection Agency's metal finishing standard that limits the concentration of seven metals, cyanide and total toxic organics (TTO) in waters that are sewered. For more information contact the MPCA's Water Quality Pretreatment Division at 651.296.6300 or 800.657.3864. Large municipal wastewater treatment facilities also deal with this regulation for industrial facilities.

Hazardous waste sludge. If wastewaters from aluminum phosphatizing operations are treated and a sludge is produced, that sludge is a listed hazardous waste [F019] and must be managed as one.

References

1. Zheng, Haixing. "An Alternative to Anodization: Sol-Gel Solutions for Metal Finishing." *Metal Finishing*, December 1998, 35.
2. Ault, Peter J. and Mike Starks. "Abrasive Blasting as an Alternative to Chromate Conversion Coating on 5086 Series Aluminum." *Metal Finishing*, July 1999, 30-33.



System layout used by Rochester Powder Coating in 1999.

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For More Information

MnTAP has a variety of technical assistance services available to help Minnesota businesses implement industry-tailored solutions that maximize resource efficiency, prevent pollution, increase energy efficiency, and reduce costs. Our information resources are available online at <mntap.umn.edu>. Please call MnTAP at 612.624.1300 or 800.247.0015 for personal assistance or more information about MnTAP's services.