RECYCLING CHEMICALS ON THE ANODIZING LINE

COST SAVINGS & QUALITY IMPROVEMENTS

presented
at the
AEC 2001
Finishing Workshop
April, 2001
Chicago, Illinois

by
Paul Pajunen, P. Eng.
Eco-Tec Inc.,
Pickering,
Ontario

INTRODUCTION

Aluminum is anodized using water-based chemicals that can be treated in a fairly straightforward manner. However, many plants now use recycling equipment to extend chemical life and reduce waste treatment costs. This is due, in part, to the large amount of solid waste that etching and anodizing generates. As most methods of recycling involve some degree of purification, anodizers often find that quality improvements go hand in hand with chemical savings. Three recovery techniques will be reviewed that are commonly used to regenerate the caustic soda etching bath, recover phosphoric acid bright dip solution from rinsewater, and purify the sulfuric acid anodizing bath.

It is well known that etching and anodizing generates large volumes of aluminum hydroxide sludge. Recycling reduces this waste, lowers chemical costs, and, frequently, improves product quality.

Aluminum dissolved in etching (1.5 mil etch)	20 lb
Aluminum dissolved in anodizing (0.7 mil anodic film)	2 lb
Waste sludge produced (15% w/w solids)	420 lb
Waste sludge produced when etch regeneration is used	64 lb
Waste reduction with etch regeneration	85%

Note: Based on 1,000 ft^2 of anodized surface area weighing about 400 lb.

1. CAUSTIC ETCH RECOVERY

Etching is caused by a reaction between the aluminum and caustic soda that produces sodium aluminate and hydrogen gas as follows:

etching reaction $2Al + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2$ (gas)

The etching process is typically responsible for 80-90% of aluminum in the waste treatment system. Chemical stabilizers (complexing agents) are added to prevent the aluminum from precipitating out in the etch tank. The additives thicken the solution to the point where enough liquid is carried out on the parts to keep the aluminum level from building up in this "never dump" etch. Rinsing carries dissolved aluminum and caustic to the plant waste treatment system.

If complexing agents are not used and the sodium aluminate concentration is allowed to rise too high, it will hydrolyze to produce alumina tri-hydrate ($Al_2O_3 \cdot 3H_2O$), thereby liberating free caustic soda.

hydrolysis reaction $2\ NaAlO_2 + 4H_2O \longrightarrow 2\ NaOH + Al_2O_3 \cdot 3H_2O$

This reaction, known as the Bayer process, is used in the primary aluminum industry to make alumina. If not properly controlled, it leads to an accumulation of a rock-hard aluminum hydroxide scale in the etch tank. By seeding the etch solution with alumina crystals in a separate crystallizer tank, it is possible to regenerate the etch solution without having scale buildup.

The basic operation of a regeneration system is such that etch solution is recirculated continuously between the etch tank and the crystallizer tank. Hydrated alumina crystals form in a slurry section of the crystallizer and settle out in the clarification section. Regenerated etch solution, with reduced aluminum and increased free caustic levels, flows back to the etch bath directly from the top of the crystallizer. Alumina crystals are withdrawn periodically from the bottom of the crystallizer and dewatered in a filter press.

Over the past ten years many large architectural anodizers have installed regeneration systems based on this process. Regeneration can reduce a plant's solid waste by over 80% while lowering caustic chemical costs by over 70%. The crystals that are removed have a variety of uses as an alumina substitute.

Crystallization systems such as the one shown here are used to continuously remove aluminum from caustic etching solutions. The aluminum is converted to a form that can be readily sold and the caustic is returned to the etch.

One issue pertaining to a regenerated etch relates to its lower aluminum levels. As high aluminum levels promote a more matte finish, there were initially some concerns that a regenerated etch would not yield a suitable finish. With dozens of systems now in operation in North America, a regenerated etch is regarded to produce a finish slightly less matte than a "never-dump" finish but satisfactory for most applications.

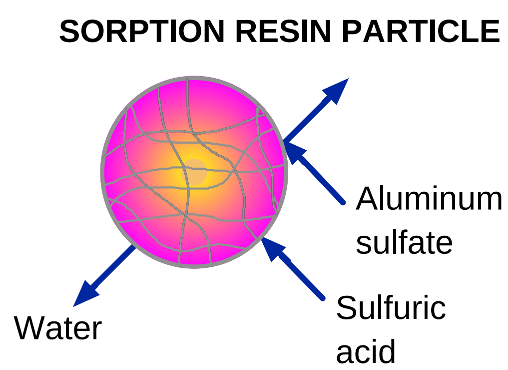
2. SULFURIC ACID ANODIZING PURIFICATION

The anodizing operation itself represents an excellent opportunity for purification. By the time the aluminum level in the acid reaches 15-20 g/L, the solution is decanted or dumped. In addition to eliminating a waste problem, continuous purification can enhance the uniformity of the anodized film.

Operating an anodizing bath in a dump/decant manner presents a number of potential problems. These become apparent due to the fact that there exists a delicate balance within an anodizing bath - namely, the relationships between the electrical resistance (caused by the formed oxide coating and the anodizing solution conductivity), the voltage being applied, and the desired constant current condition. The electrical resistance increases relative to the thickness of the oxide coating and to the increasing aluminum concentration in the anodizing solution. To compensate for this increased resistance, the rectifier voltage must be increased in order for the current to remain constant. Adding in other variables such as bath temperature, degree of solution agitation, and sulfuric acid concentration can result in upsets and potentially lead to a decline in product quality.

Maintaining a consistent, low aluminum concentration removes or minimizes a variable that can affect the balance between resistance, voltage, and current. Controlling the aluminum concentration and recovery of sulfuric acid for continued use in the aluminum finishing industry has been practiced for a number of years. The end result is ensuring a consistent, predictable bath operation leading to cost savings and improved product quality.

Acid sorption technology employs specially treated ion exchange resins that have the ability to sorb free (unused) mineral acids while rejecting the salts (e.g., sodium sulfate) of these acids. The most unique feature of these resins is their ability to release the acid with a simple water wash.



A popular method of acid recovery employs a process called acid sorption (APU). Over 400 systems using this technology are currently in operation worldwide.

A standard APU offering for aluminum anodizers, known as AnoPur™, is a pre-assembled, skid mounted device that is fully tested, with resin, prior to shipment. The resin column is mounted on a stainless steel frame with process valves, internal piping and a control panel. The panel includes a PLC-based control system.

3. BRIGHT DIP RECOVERY

Concentrated phosphoric acid solutions, usually with additions of nitric acid, diammonium phosphate and copper, are used to chemically brighten aluminum parts. After brightening, the adhering solution must be rinsed off immediately with water. Due to the high acid concentrations and viscosities of bright dip baths, carryout of bath solution on the parts is typically 3-4 times greater than from an anodizing tank. While aluminum contamination of the bath is rarely a problem, there is a substantial loss of bath chemicals.

Most plants collect the rinsewater as a 35% solution for resale as fertilizer. The seasonal and regional variations in demand for the rinsewater reduce the value to between 10-20% of the original chemical cost.

The rinse can be reconcentrated to bath strength with a vacuum evaporator; however, a purification step must be employed to prevent aluminum buildup. A combination cation exchanger resin bed and an acid sorption rein bed undertake this purification step. This combination is known as a DPU. The cation resin bed removes about 90% of the aluminum before the solution flows to the evaporator. This resin bed is regenerated with sulfuric acid and the waste, containing sulfuric acid and aluminum, is processed with the sorption resin bed. Purified sulfuric acid is maintained within the system for use in the next regeneration cycle.

This phosphoric acid recovery system was designed to recover over 2000 tons of 80% acid per year. The vacuum evaporator is located on the right side. To the left is the purification equipment. The cooling tower was roof mounted.

By using the DPU system, the cost of operation is reduced to the point where recovery becomes economical for any plant consuming more than two truckloads per month of 80% acid. Several installations have been installed over the last fifteen years and, in all cases, acid recovery efficiencies in excess of 85% have been reported.

CONCLUSION

With the increased focus on environmental concerns in all facets of business, anodizers can look at a number of opportunities in their plants that will reduce process chemical costs, reduce waste treatment chemical and labor costs, and, in many cases, enhance product quality. Recycling is an environmentally pro-active step that demonstrates a responsible corporate image to your customers, employees, and to the local authorities.