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.

There are three commercially available methods that deal with the dissolved metal problem.

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

1. 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.

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1 Note that each of these technologies work best with dissolved metals that form a positive ion in solution (Fe³⁺, etc.). Metals that form a negative ion complex (TiF₆⁻³) are very difficult to remove with a reasonable efficiency in any of the methods discussed.
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.

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

2. **Diffusion dialysis**

The diffusion dialysis process makes use of a membrane that allows the acid’s negative ions (SO$_4^{2-}$, NO$_3^{-}$, Cl$^-$, etc.) to pass through while preventing the positive metal ions (Fe $^+$, 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.

Diagram showing the process by which diffusion dialysis recovers acid (diagram provided by Mech-Chem Associates, Inc.)
3. **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.
The acid sorption process is commonly used in large aluminum anodizing systems to maintain the amount of dissolved aluminum in the correct range. It is also often used for stainless steel pickling operations to recover the nitric-hydrofluoric acid solutions.

**Economics**
The economics will determine which of the three methods of acid recovery makes sense for each metal finisher. That is why it is critical to know the cost of acid purchases and acid disposal to determine the payback for acid recovery systems.