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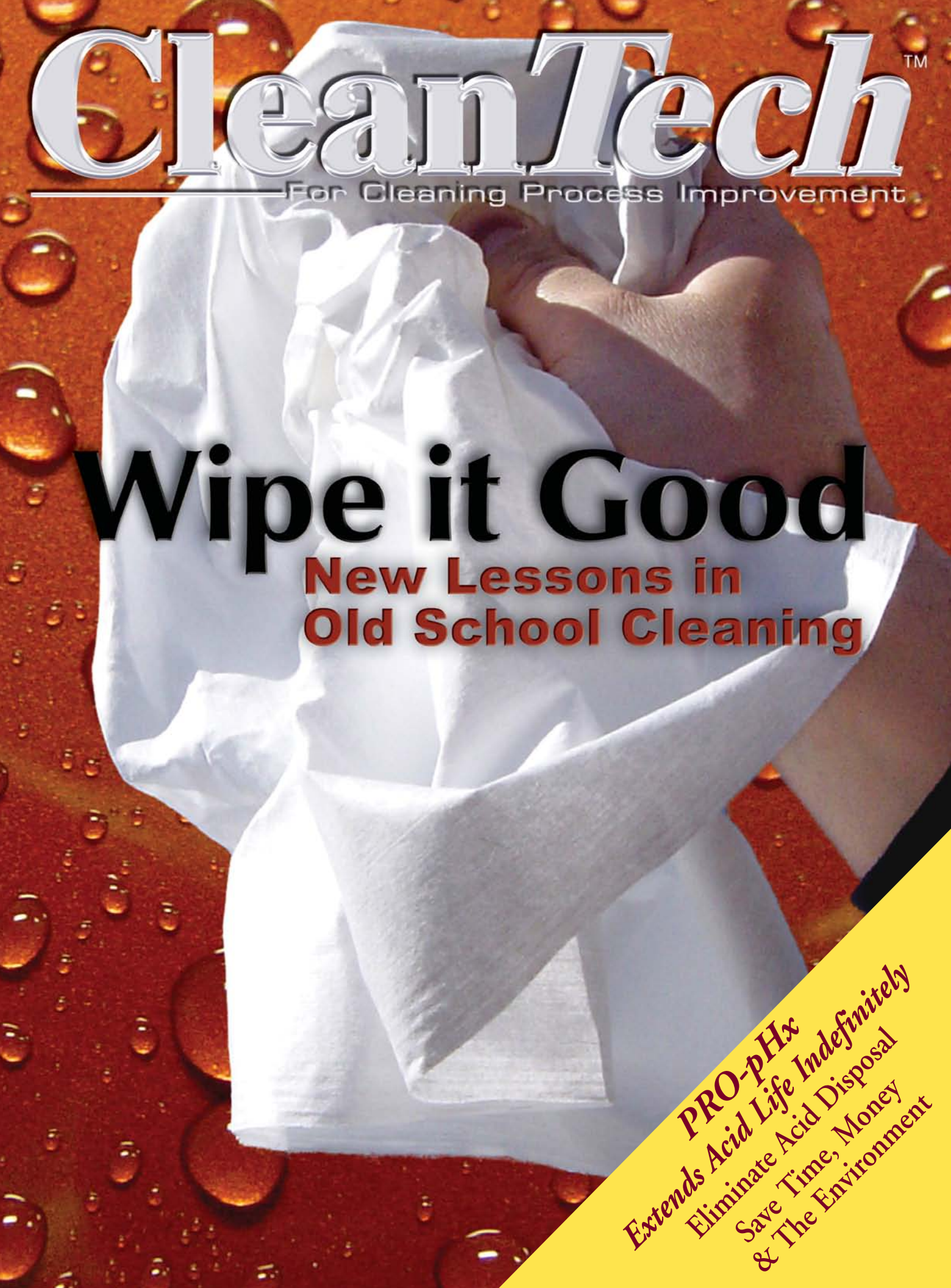

Wipe it Good

New Lessons in Old School Cleaning

The Acid Test

by David French

According to U.S. Environmental Protection Agency data, industry in the U.S.A. uses more than six billion gallons per year of various virgin acids to pickle, clean, activate or passivate metal and plastic surfaces. And because a typical acid bath is 50 percent by volume, (50 percent acid plus 50 percent water), the actual amount of contaminated acid requiring disposal could exceed 12 billion gallons per year. Over time these acids become contaminated with metals and organics and require treatment or disposal at a considerable expense, as hazardous or non-hazardous waste. These spent acids could be contaminated with organics, iron, lead, zinc, nickel, copper, cadmium, aluminum, trivalent chromium, hexavalent chromium and other metals.

The manufacture of quality finished products in the metals processing industry generally begins with the removal of soils and oils with solvent, alkaline or acid cleaning solutions. After rinsing, the parts are exposed to an acid to remove mill scale or to activate the surface for subsequent plating, painting or coating. Acids contaminated with oils or dissolved metals do not allow subsequent finishes to be applied to specifications. For example, in the cold forging industry, oily blanks are placed in a barrel. The processing steps include alkaline cleaning, rinse, acid pickle, rinse, zinc phosphate and lube. The blanks are then removed from the barrel for cold forging into the finished product. If mill scale is not removed by the acid, the proper amounts of phosphate and lube cannot be applied and the blanks will cause seizing in the forge.

Historic practices are to dump the cleaners and acids; this practice frequently causes wastewater treatment problems, which lead to effluent compliance issues. Technologies such as ultra-filtration and bacterial systems have been used for years to prevent alkaline cleaner dumps. Technologies such as distillation, ion retardation, crystallization and diffusion dialysis are proven to purify acid solutions.

Unfortunately, these acid purification processes are capital intensive, energy intensive and sometimes difficult to integrate into the manufacturing and maintenance schedules. Capital costs can start at $50,000 and can increase to $500,000, depending upon the type of acid and volume to be processed. A typical acid purification process consists of:

1. Distillation – Volatile acids are distilled off and condensed leaving the metal impurities in concentrated form for ultimate disposal.
2. Ion Retardation – The resin absorbs free acid (i.e. HCl) but passes the contaminant (i.e., $FeCl_3$). The acid is desorbed (regenerated) with water.
3. Crystallization – Hot H_2SO_4 contaminated with $FeSO_4$ is cooled to form insoluble $FeSO_4$, which is removed via a filter press or centrifuge. The purified acid is reheated for reuse.

Table 1: Chemical Purification Advantages

Eliminates decants/dumps of acids

Reduces acid purchases 30% - 50%

Reduces hazardous waste generation 20% - 50%

May result in small generator classification

Eliminates on-site treatment or off-site disposal

Reduced caustic consumption for neutralization

Improves plating quality and reduces rejects

Reduces production downtime

Protects downstream plating baths

Capital investment is simple filtration

4. Diffusion Dialysis – An anionic membrane allows free acid to pass through the membrane but contaminants (i.e., $FeCl_3$) are rejected.

In 1999, a catalyzed silica reagent (a catalyst compound attached to soluble silica) named PRO-pHx was introduced to the electroplating industry. This chemistry is currently being used in the electroplating, electropolishing, anodizing, plastics, gravure, cold forming, galvanizing and wire forming industries to purify the acids, which eliminates the need to dump these acids to wastewater treatment and/or off-site acid disposal. The chemistry is used at one percent of the bath volume and simple cartridge filtration is used to remove precipitated organics and metals.

For medium to large filtration systems, the Serfilco Ltd Mega-Flo pump/filter works well. The chemistry is currently being used in hydrochloric, sulfuric, nitric, citric, formic, hydrofluoric, phosphoric and acid salt baths. These acids are used in cleaning, stripping, pickling, activation, and passivation of various metal and plastic surfaces. Industries such as electroplating, galvanizing, cold forming, steel, wire and anodizing all use these acids. Table 1 lists the advantages of this method of chemical purification.

Over 500 acid baths in 220 industrial plants are currently being treated with this chemistry. The following case histories are typical of results being obtained.

Case in Point

Thermal Metal Treating, Inc. – Aberbeen, North Carolina

Thermal Metal Treating (*www.thermalmetal.com*) is a commercial heat treating and industrial coating firm that services the automotive, medical and computer printer industries. They use HCl to pickle and activate carbon steel and stainless steel and to strip zinc coatings from various metals. The acid purification chemistry was started in October, 2001 and no acid solutions have been dumped or decanted since that date.

An additional benefit has been the 94 percent reduction in the generation of listed hazardous wastes. This is due to the fact that the chemistry precipitates the toxic metals in the acid bath as a dense precipitate, which prevents the metals from forming water loving hydroxides in the wastewater treatment system. For instance, when a soluble iron ion is neutralized with caustic soda, iron hydroxide $Fe(OH)_3$ is formed. This molecule is then dewatered in a filter press. Unfortunately, the filter cake is typically 70 percent water and 30 percent solids (iron hydroxide).

Table 2 lists the results Thermal Metal Treating has realized. Mark Scott, Vice President at Thermal Metal Treating, states, "Using PRO-pHx and filtering the acids has lowered our operating costs, reduced our hazardous waste generation and eliminated independent lab testing previously required by the regulatory authority."

Saporito Finishing Company – Chicago, Illinois

Saporito (*www.SaporitoFinishing.com*) is a large job shop plating company that performs electroplating, anodizing, passivating, black oxide, phosphating, magnesium finishing, conversion coating and electroless plating finishes, as well as vibratory deburring, ball bearing burnishing, and blasting. Saporito's acids have been purified using the chemical reagent process since June 2002. Saporito uses AA analyses to track the metals contamination in their acid baths weekly. Wet analysis in Saporito's chemistry lab is performed weekly and shows consistent acid concentration.

Saporito's first application of the precipitation chemistry was on an 800 gal HCl bath on an acid zinc rack line on August 19, 2002. The acid was previously dumped every three months. After addition of the chemistry and filtration, the acid has not been dumped in more than 30 months. The acid bath is filtered with five 20 inch 5-micron polyspun cartridge filters. Filters are changed weekly depending upon the production load. Analysis of the acid bath for copper, nickel, cadmium, chromium and zinc shows stable values over the 30 month period.

The above results encouraged Saporito to use the chemistry in an 800 HCL bath on the rack cadmium/zinc nickel line on July 21, 2003. Prior to the purification chemistry, this bath was dumped every 11 weeks. The bath has not been dumped or decanted in over 84 weeks.

The third application was in a 250 gal HCl bath on the electroless nickel line. This bath was previously dumped every three weeks and has not been dumped in over 76 weeks. Saporito technical personnel and

their EPI chemical supplier continue to apply this purification chemistry to more of the acid tanks. Table 3 lists typical analytical data on the zinc line A from August 15, 2002 to November 25, 2003.

Conclusion

Companies that purchase caustics and acids for alkaline cleaning and pickling need to utilize Pollution Prevention (P^2) technologies to minimize wastes, to reduce production costs and to improve the environment. Membrane and biological systems are proven to eliminate alkaline and acid cleaner dumps. The catalyzed chemistry has been proven to eliminate acid dumps. Utilization of these two pollution prevention technologies will reduce manufacturing costs, improve product quality, and improve our environment for generations to come.

Table 2: Thermal Metal Treating Results

96% reduction (by weight) in hazardous waste

Reduced production downtime

Reduced HCl and NaOH purchases

Reduced water consumption for rinsing

Reduced labor and chemical usage in waste treatment

Table 3: Saporito Analytical Results – Zinc Line A 8/19/02 – 11/25/03

	RANGE	AVERAGE
Copper, ppm	9.4 – 17.0	12
Nickel, ppm	.98 – 56.5	22
Cadmium, ppm	1.4 – 89.0	35
Chromium, ppm	1.4 – 56.0	40
Zinc, %	1.6 – 4.2	3.0

About the Authors

David C. French was President of Amplate Inc. of Charlotte, NC and is now President of David French & Associates, an Environmental Consulting and Manufacturing Brokering Firm, and the Vice President of Technical Sales for PRO-pHx, Inc. Mr. French has 29 years experience in Plating and Machining Manufacturing. He is a recipient of the NC Governors Award for Waste Reduction in Manufacturing and has been heavily involved in P^2 Technologies since 1998.

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