


PRO•pHx Acid Life Extender

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The following is condensed from a paper given at the Aerospace/Airline Plating Forum in Tulsa, OK.

Lean & Green Manufacturing

Lean and Green manufacturing involves many factors. One of the most important factors is reducing the volumes and costs of chemicals used in the production process. Industry uses acids for surface activation (electroplating applications), stripping (electroplating and metal finishing) and pickling to remove iron oxide mill scale (galvanizing, steel/wire). When these acids become contaminated, the acids are treated on-site or hauled off-site for disposal. This is at a substantial cost to industry.

The late Dr. John Wagner devoted his professional career to the study of inorganic catalyzed reagent chemistries. His discoveries have found applications in the wood preservation industry, certain site remediation projects and in the purification of organic and inorganic acids. The focus of this paper is the application of this proprietary catalyzed reagent for the purification of acids in the metal finishing industries.

The catalyzed reagent is a proprietary blend of soluble silicates, which allows for the effective immobilization of soluble metals by reacting with them to form insoluble metal silicates and insoluble oxides. Soluble silicates are a unique class of polymeric compounds in which sodium oxide (Na₂O) is associated with silicon dioxide (SiO₂) generally in ranges varying from 1:1 to 1:3.22. These depolymerize in dilute solutions to form chains of silica and oxygen. With negative charges on some oxygen, reaction occurs with metal ions having positive charges to form stable, insoluble metal silicates and oxides..

Early Commercialization

Gwen Wagner began marketing the chemistry in 1999. The first commercial application was at Amplate in Charlotte, NC. Over a period of 9 months, the chemistry was added to all acid baths. None of these acid baths have ever required waste treatment.

The next use of the chemistry at Amplate was the application to acid and alkali rinse waters. With pH adjustment to 7.6 and appropriate filtration, Amplate was able to go to zero discharge on these rinses. The chemistry was later applied to zinc rinses, which also resulted in zero discharge. Chromate rinse waters containing Cr⁺³ and Cr⁺⁶ were also segregated and treated with the chemistry with mixed results. Amplate discontinued the use of their ion exchange and electrocoagulation systems and replaced them with the reagent chemistry and standard filtration.

Current Applications

The chemistry is currently being used in approximately 150 electroplating plants, 3 anodizing plants, 1 wire plant, 2 galvanizing plants and 1 steel pickling plant. The following data is typical.

1. Canadian Electro Galvanizing plant – rack line:

This plant uses 40% HCl in a 350-gallon tank to remove mill scale and to activate the metal surface for their pipefittings. This plant dumped the bath weekly when the iron concentration reached 4%. The plant has been using the catalyzed reagent chemistry and has not dumped the bath in 14 months. The average iron concentration has stabilized at 2.8% Fe. A Flo-King filter is used to remove the iron precipitate and the filter is cleaned daily. Cost savings of \$9,654 USD have been verified and these savings do not include reduced downtime and reduced amounts of F006 filter cake generated.

2. Illinois Electroplating Plant – rack Zn line: - DuQuoin

This plant previously used 30-50% HCl for surface activation and dumped 55 gallons per day of the partially spent acid to waste treatment. The addition of the chemistry was made in early 2004 and no acid dumps have occurred. In addition, the plant has reduced the bath concentration to 20-30%, while maintaining required quality control. Acid consumption has been reduced by 50% with similar reductions in caustic neutralization costs and hazardous waste generation. Acid makeup is 12 gallons a day and 1 quart a day of catalyzed reagent is used.

3. Connecticut Electroplating Plant – barrel Zn lines: - Thomaston

This plant has used the chemistry since March 1, 2003 in a 220 gal 30% HCl bath and a 10% H₂SO₄ bath. The HCl bath was previously dumped two to three times a week and the H₂SO₄ was dumped daily. The baths have not been dumped in 12 months. Since the chemistry removes iron in the acid tanks, iron contamination in the zinc-plating tank is reduced. Previously, the zinc bath was treated with HMnO₄ three times a week and is now treated once every two weeks. The HCl tank is filtered with one 20" cartridge, 10-micron filter that is changed weekly.

4. North Carolina Electroplating Plant – Aberdeen

This plant uses HCl for pickling and activation of carbon steels and stainless steels and or stripping of zinc coatings from various base metals. Plant processes include stainless steel black oxide, ferrous metal black oxide, zinc phosphate, iron phosphate and manganese phosphate heat-chemical coatings.

The plant has utilized the chemistry since October 2001 and the two HCl tanks have not been dumped since that date. Plant records indicate:

- 95% reduction in F006 hazardous waste/ Reduced HCl usage/ Reduced NaOH usage
- Reduced plating system downtime for maintenance/Reduced wastewater treatment costs
- Reduced rinse water contaminants

A simple pH neutralization system is currently being installed to close loop the acid & alkaline rinses. This will be the subject of a future paper.

5. Georgia Electroplating Plant - Valdosta

This client has a 500 gallon 40% V/V HCl tank used to strip chrome from steel, stainless steel, aluminum and yellow metals. Previously, stripping times were erratic due to dissolved metal concentrations and oily film on the acid tank.

The chemistry has eliminated the oil in the strip tank and stripping time has decreased due to consistent acid bath quality, purity and strength. This plant has been using the chemistry since 2003; and the acid baths have not been dumped and copper immersion plating has not occurred.

6. George Plating Shop - Toccoa

This plant plates large quantities of yellow metals, which causes copper to build up in the HCl and H₂SO₄ tanks. Both acids were used at 20% V/V concentrations and the HCl tank was dumped 3 times a year and the H₂SO₄ tank 4 times a year due to copper immersion plating problems.

7. Indiana Electroplating Plant – Fort Wayne

This company does semi-bright/bright nickel and trivalent chrome plating. The 1,000 gallon 20% HCl tank was previously dumped monthly and has not been dumped in that last 12 months. The plant manager estimated acid and caustic savings of over \$6,000 a year. The filtration consists of five 20" 30-micron cartridges that are changed once a week. The generation of F006 hazardous waste has been reduced.

8. Canadian Hot Dip Galvanizing Co.

This galvanizing company began using the chemistry on a 3,000 gallon 20% HCl pickling tank in May 2003. Prior to using the precipitation chemistry, the iron concentration would increase to 6% Fe within 3 months. The cost to dispose of this bath was \$5,000 CND or \$20,000 CND per year.

Using the catalyzed reagent, the reagent cost to make the initial 1% charge on the 3,000 gal tank is \$2,430 for 30 gallons of reagent. On an annual basis, this tank will consume approximately 3,350 gallons of 32% HCl, which requires 33.6 gallons of reagent. The total first year reagent cost is \$5,150 as compared to a disposal cost of \$20,000. Second year reagent costs are projected at \$2,720 a year, which would give an 86.4% savings. The operating cost for filters and the amortized cost for the filtration system are not included in these savings.

Over the last ten months, the iron concentration has gradually increased and stabilized at 7% Fe. Because the acid is clear and free of organics, the customer reports superior pickling

results at this higher Fe concentration. String wold cartridges were originally used and later changed to poly spun cartridges, as this reduced the iron concentrations by 2%. A 15 cartridge 20-micron filter is used with weekly cartridge changes.

The customer also reports another important benefit. The amount of iron drag out into the flux tank has been reduced, which reduces the solids formation in the flux tank. This has reduced the maintenance time to clean the flux and has contributed to more consistent quality control of the galvanized parts.

This facility has approximately 98,000 gallons of pickle acid in the plant. By using the savings demonstrated on the 3,000-gallon tank, projected annual savings could approach \$480,000 a year.

9. North Carolina Captive Shop – Charlotte

This plant uses 40% nitric acid and 10% ammonium bifloride in one 500-gallon etching tank and 15% citric acid in the 500-gallon passivation tank. Dumping frequency would vary from 2 to 3 times a year. The acids are used in the stainless steel passivation line. When the acid was new, passivation time was 20 minutes but would lengthen to 120 minutes before dumping the acids.

The acid purification chemistry is now being used and passivation times remain constant at 20 minutes. The same quantity of work is now being passivated in 446 hours as compared to the previous 1,560 hours for a reduction of 70% in production time.

Savings in acid and caustic consumption are calculated at \$8,300 a year with additional savings in waste treatment, operator time, reduced F006 amounts, and reduced utility consumption in the wastewater treatment plant.

10. Tennessee Rack and Barrel Operation – Memphis

This company began using the chemistry in June 2003 in one 1,000 gal HCl tank. Later, the chemistry was added to another 1,000 HCl tank, a 3,000 gal HCl tank, and a 750 gal HNO₃ tank. None of these tanks have been decanted or dumped in over 9 months.

Over a 6-month period of using the chemistry, caustic consumption dropped 46.3%, HCl consumption dropped 70.8% and hazardous waste generation dropped 34%.

The following table gives actual savings:

Item	6 Months Data		
	Before Chemistry	After Chemistry	Savings
50% NaOH	\$14,244	\$9,324	\$4,920
20o Be HCl	\$26,248	\$7,651	\$18,597
Hazardous Waste	\$8,178	\$5,400	\$2,778
		Total Savings	\$26,295
		Less Chemistry	\$6,660
		Net Savings	\$19,695

The NET savings do not include:

Reduced operating costs on sludge drier. Better plating due to better acid quality control. No production downtime due to dumping. No acid dumps to batch treat – labor savings. Improved activation due to lower metal concentrations. Lower TDS to the POTW.

Summary and Conclusion

The catalyzed reagent has been used commercially for over 3 years in over 150 plant locations. Economic and environmental benefits have been substantiated by plant operating personnel and these benefits can include the following:

Elimination of Acid Dumps/Eliminate On-Site Neutralization of Off-Site Hauling
 Increased Pickling or Surface Activation Rates/ Reduced Fuming from Hot or Ambient Acid Baths
 Reduced Contaminants in Rinse Waters/ Reduces Environmental Liabilities
 Elimination of Production Downtime Due to Tank Dumps/ Lowers Acid Concentrations
 Minimal Capital Investment – Filtration only/ Reduces Dissolved Solids to Wastewater Treatment

Possible Change to Smaller Quantity Generator Status/Helps Attain “Near Zero” Discharge
Reduces TSS and TDS Loadings to UF&RO Polishing Systems/ Removal of Organics

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