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**ENVIRONMENTAL CHALLENGES**

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# Acid Pickle – Miracle Drug!!

## Introduction

An article appeared in the March 2005 issue of Plating and Surface Finishing (AESF) which I looked at, considered it to be a 'bit of black magic' and did not take it seriously. It was about an ***acid extender*** system for acid pickles, including hydrochloric and sulphuric acids, that dramatically extended the pickling bath life by precipitating out the iron and zinc in particular and releasing otherwise spent acid for re-use in the pickling bath. The acid pickles were said to last ***indefinitely.***

I filed the article away and, of course, forgot all about it.
Earlier this year, via an unlikely set of circumstances, I came across a local company who was seriously considering the use of this system. I visited the plant for a '*walk through eco-audit'* and was shown a few technical papers on this system. One of the paper authors was Ken Lemke, a former colleague of mine at M&T Chemicals (now Atotech) who now is the President of Canadian Finishing Systems. Because I hold Ken in high regard, I read his and other articles and sent off emails in all directions to see if it was sound technology or just wild imagination of a chemist in his laboratory. I have been around long enough to be skeptical about new '*wonder additives'* in the Metal Finishing industry.

Spent acid pickles have been a real problem for the industry in respect to both disposal and possible recovery for re-use. There has been some success with expensive ion exchange recovery systems and there have been many attempts at evaporation recovery systems – some which do work technically and industrially but not economically.

## Basic Technology

The chemistry is based on silicates, was developed by Dr J Wagner around 1989 and was first used commercially at a company called 'Amplate' in the US in 1999. The initial baths using the system lasted over 4 years without dumping and/or replacement which is quite outstanding as they are normally thrown out and changed every few weeks.

Silicate chemistry is quite complex and not altogether unrelated to carbon chain chemistry. It is not the purpose of this article to try to baffle everyone with chemical equations but rather simply refer to some of the basics involved.

There has been a lot of argument for many years in regard to the best free acid strength for pickling – most electroplaters and galvanizes use hydrochloric or sulphuric at between 10 and 30% free acid. Some claim that low free acid (around 5%) and high acid salt (250 g/l iron chloride or sulphate) works well too as the acid salt contributes to the pickling action and high free acid tends to attack the base metal excessively. A lot of operators follow the 'Kleingam curve for controlling the ratio of free acid to acid salt and the aggressiveness of the pickle. It is very common for operators to continue to add concentrated acid well after the bath is overdue for changeover. This activity can just be a waste of time and money.

Acid pickles remove rust, scale, oxides, some base metal and loosen some embedded organics as well. The net result is that the free acid drops and acid salts rise to a point where more straight acid additions do not effectively increase the efficiency of the pickle. At this stage, most operators drop the pickle and make up a new one.

The recently released silicate system comprises of a blend of catalyzed materials, predominantly soluble silicates that stabilizes the dissolved metals and decomposes some organic hydrocarbons. They react with polyvalent metal contaminants in the acid pickle solutions to form insoluble (precipitated) silicate complexes that are stable over a wide pH range and resistant to leaching.

For those more chemically minded, soluble silicates are a unique class of polymeric compounds in which sodium oxide ($Na_2O$) is associated with silicon dioxide ($SiO_2$) in a wide ratio range. These chemicals depolymerize in dilute solutions to form complex chains of silica and oxygen. Negatively charged oxygen ions then react with metal ions to form stable, insoluble silicates within the chain system.

The system also reacts with and destroys several volatile and non-volatile organic compounds – more details are available from the vendors.

So, the net effect is that insoluble metal silicates are formed in the bath, which in turn, release the otherwise reacted acids for actual pickling which was the original intent.

The build up of precipitated silicates is continuously removed by filtration, leaving the pickle bath clean and free to continue performing well. Really, the only virgin acid additions required are to replace drag-out and evaporation losses and the pickles seem to last indefinitely – no down time for dropping the spent pickle and making up a new one. The sludge precipitated by this system is very dense and is generally non-hazardous (except for any entrapped free acid) and the precipitate passes the TCLP leaching test as required by the US EPA.

The pickling speed remains the same or is actually enhanced because the pickle tank is cleaner. Many users have found that they can operate at lower free acid levels with this system.

## <u>**The Environmental Hooks**</u>

I am sure that they have become perfectly obvious already.
We will only comment on the major environmental benefits here.

a) **Resource use efficiency** - Pickling acid requirements can be reduced by more than 30% (often much higher) and acid disposal costs by up to100%. The acids are continuously freed up to do their pickling job rather than being turned into acid salts, thus dramatically increasing the use efficiency of the acid. Materials use efficiency is becoming a very popular issue in industry generally.

b) **Compatibility with other pickle addition agents –** Commercial tests have shown that many pickle corrosion inhibitors still work well with the system. Care needs to be taken to ensure that some specific organic additives are not destroyed by the catalytic reactions. The same argument applies to several anti-vapour additives (fume suppressants), which are often necessary to reduce equipment and building corrosion as well as making the production line safer for the operators. This is a big advantage in hot dip galvanizing where the acid pickle fumes are perhaps the major pollutant source, not the dense white fumes of ammonium chloride as many environmentalists seem to think – it looks bad but is relatively harmless. An effective fume blanket on the pickle surface can prevent the acid fume problem.

c) **Waste Treatment (***hate those words***) Reduction –** If we are not throwing valuable acid down the drain, we do not incur the use of caustic soda to neutralize it to the regulatory standards. This also means that there will be less sludge to dispose of – ie. the sludge generation from mixing spent cleaners and spent acid pickles for self neutralization of pH. There may be some compromise situations here because many plants still do use their waste cleaners to neutralize the spent pickles and also use the convenience of cleaner drag-out (to the floor) to neutralize the acid drag-out (also to the floor). In terms of efficient and sustainable operations, such wastes should be looked on as potential resources lost and money down the drain instead of the very easy and convenient neutralization. There are several alternatives to obviate this problem:
   (1) – use long life alkali cleaning systems or cleaners that can be continuously regenerated or rejuvenated
   (2) – utilize the waste alkali for other neutralizing purposes within the plant
   (3) – sell the waste caustic to other companies for their neutralization requirements.
   (4) – reduce the drag-out from both the alkali cleaners and the acid pickles via better draining, multiple counterflow rinsing and prevention of floor losses. This is especially critical for hot dip galvanizers because they conventionally, have very poor rinsing and very high drag-out volumes. This can have a significant detrimental effect on the economy of using this new silicate system, particularly if most of the work is tubular.

(5) – use other forms of pre-cleaning – biological, acid based or vegetable oil based

d) **Sale of Recovered Metal Bi-products –** well one at least for galvanizers. We have all been astounded at the metal price hike in recent years. Zinc was below A$1 per kg just a few years ago and now it is over 5. The insoluble zinc silicates represent reasonable value for metal recovery. The debate is still out as to whether the zinc should be separated from the iron for re-sale and this may vary from place to place. We would recommend that they are separated which will mean dedicated pickles for pickling steel and stripping off zinc and are confident that the iron silicates could be sent to steel mills – probably donated free of charge but this is far cheaper than paying for it to be discharged at a landfill. For electroplaters, it is advisable to have a separate pickle for every base metal used which would provide for segregation of the precipitated silicates and easier resale. The filtration technique is critical, especially for metal recovery. Initially cartridge filters were used and replaced frequently. Now the trend is towards automatic backwash filter press systems, which are expensive and should be taken into account when doing the economic evaluation.

## Applications

The system can be used for most acid pickle solutions – electroplating, hot dip galvanizing, de-oxidizing, etching, electropolishing, steel pickling mills and wire plants, anodizers, etc.

Acids used include Sulphuric, Hydrochloric, Nitric, Phosphoric, Citric and blends and is effective in controlling the build-up of organics and metals including iron, zinc, copper, aluminium and others.

The product is inorganic, odourless, has no fumes or outgassing and meets the OSHA – 20 non-hazardous specifications.

For hot dip galvanizing applications, another advantage is that there is less carry over of iron contamination into the flux bath

## Economic Investment Pay-back

This needs to be calculated carefully as it will vary for different applications and different operating lines.
It also depends on the cost of raw materials and the discharge costs for liquid and solid effluent streams.
It is possible to calculate a reasonably accurate expected pay-back period for each application and we would advise each potential user to do this.
The projected savings include:

- reduction of acid purchases
- reduction in effluent neutralization

- reduction in disposal cots – liquid and sludge
- possible sale of zinc sludge
- reduction of down time and effluent plant operation

The new costs would include:
- initial and maintenance additions of proprietary chemicals
- cost and maintenance of the filtering system

There will be a loss in the first year because of the initial dose of proprietary chemicals to the bath and the cost of the filtration unit (could be written off over several years).

## Commercial

The commercial system on the market is called **PRO-pHx** from PRO-pHx, Inc USA. There are about 450 customers worldwide with around 90% of them being electroplaters. This 90% only constitutes about 20% of the sales volume because the tanks are small when compared to galvanizers.
The proprietary product is used by adding around 1% (by volume) to a new acid bath and installing the filter. The bath is monitored for acid concentration and regular additions of acid and proprietary product are made to maintain the proper levels and replace materials lost through drag-out. The product is not effective at less than 0.5% concentration in the pickle bath.

## Conclusions

It does pay to be cautious and perhaps, initially skeptical about radically new *super chemicals* but, in this case, there are already over 450 customers and several written case studies to argue about the positive gains and advantages of this system.

In terms of Cleaner Production or Pollution Prevention, it provides for more efficient use of resources, reduces waste at the source, reduces wasteful effluent treatment and offers possible resale of valuable bi-products. It is compatible with typical existing metal finishing lines, is economically feasible, socially acceptable and environmentally friendly.

With an eye to the future, it appears to the author that a combination of this technology with biological degreasing, would create a giant step forward in our industry towards environmental sustainability and greatly improve the environmental image of the trade.

NB. This product will be available from a local agent in China real soon.