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A Practical Approach to Hydrochloric Acid Pickling Prior to Zinc Plating

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With the emphasis on production schedules and keeping the plating bath in optimum condition to produce bright parts, the hydrochloric acid pickle is probably the most ignored part of a zinc-plating line. There seems to be no standard method of maintaining a pickle bath. For instance, some pickle solutions are changed once a week, whereas others may be changed only twice a year, and certain pickles are never changed. It is common for platers to periodically take a portion of the old pickle solution out and replace it with fresh acid.

Many platers do not control the acid content of their pickle solutions, and there are still a large number who simply guess at the concentration. This general lack of attention toward hydrochloric acid pickle baths is understandable since very little has been written on the subject. (There has been a limited amount of literature directed toward sulfuric acid pickling but not relating to zinc plating.[1-5]) Table I describes several pickle baths that are commonly used by zinc platers for various ferrous-based substrates.

WHY SHOULD A PLATER KNOW MORE ABOUT A PICKLE BATH?

Let us first address the need for a plater to know more about the pickle bath. The first and most obvious reason is that weak pickle baths do not sufficiently remove scale and rust from parts. On the other hand, overpickling etches parts and makes it more difficult to achieve brightly plated work and increases the chance for hydrogen embrittlement to occur. Since it is beyond the scope of this article to discuss hydrogen embrittlement, we suggest you read a recent article by Altmayer.[6] In addition to these reasons, it is extremely important for a plater to realize that a pickle bath is a primary source of contamination for the plating bath. Drag-in of contaminants from a pickle causes plating rejects and waste treatment problems that can be avoided with a better understanding of pickle bath life and control.

Table II. Methods of Analysis for Acid Concentration in Hydrochloric Acid Pickle Baths [a]

pH Method:

1. Pipette a 5.0-ml sample into a 250-ml Erlenmeyer flask.
2. Add 50 ml of distilled water.
3. Titrate with 1.00 normal sodium hydroxide to pH of 4.

Calculation: (mls 1.00 N NaOH) × 1.973 = % concentrated HCl in pickle

Indicator method:

1. Pipette a 5.0-ml sample into a 250-ml Erlenmeyer flask.
2. Add 2–4 drops of methyl orange indicator.
3. Titrate with 1.00 normal sodium hydroxide to a color change of orange to green.

Calculation: (mls 1.00 N NaOH) × 1.973 = % concentrated HCl in pickle

[a] The concentrated HCl as received is considered 100% even though it may be designated as 37% when purchased.

ANALYTICAL CONTROL OF HYDROCHLORIC ACID PICKLE BATHS

Control of the acid concentration of hydrochloric acid pickle baths is quite simple, and one does not need to be a degreed chemist to perform the analysis procedure. The methods in Table II require some very basic glassware and pH indicators or, preferably, a pH meter. Incidentally, every chloride zinc plater should have access to a good pH meter. pH papers are sometimes used but are not reliable enough for pH control of a chloride zinc bath.

Contaminants in a pickle bath can easily be quantitatively determined by atomic absorption spectroscopy. There are many analytical labs that will do this for a nominal fee. Often, plating suppliers will offer this as a free service for their additive customers. The most common contaminants are iron and chromium. Analyses for these contaminants are not something that need to be done on a daily basis but should be done often enough to enable a plater to set guidelines for how long a pickle should be used before requiring change.

EFFECT OF CONTAMINANTS ON ZINC-PLATING BATHS

As you can see from the wide range of results in Table III, the amount of dissolved iron is generally quite high in the pickles tested. It is interesting to note that three of the platers were not sure how old the pickle solutions were.

Table I. Hydrochloric Acid Pickle Baths for Various Ferrous Substrates

Type of Part	*Percent by Volume Concentrated Hydrochloric Acid Generally Used*	*Other Ingredients*
Carbon steel	30–40[a]	Usually none.
Heat-treated steel	20–30	An inhibitor to prevent black smut from forming on the surface of the part.
Cast iron	≤20	An inhibitor to prevent opening of pores that may trap solution, which can bleed through and cause corrosion.
Cast iron	≤20	1 lb/gal of ammonium bifluoride to help dissolve embedded sand from the mold.
Leaded steel	20–30	An inhibitor to prevent attack on the steel, leaving lead on the surface of the part.

[a] 30% is the strength requested by several automotive firms to minimize the chance for hydrogen embrittlement.

Table III. Typical Analytical Results for Pickle Baths in 12 Chloride Zinc Plating Lines [a]

Type of Operation	Bath Volume (gal)	Fe (ppm)	Cr (ppm)	Age of Pickle	HCl Concentration (%)
Automatic return rack	10,000	1,000	88	3 weeks	48
Automatic return rack	2,400	1,880	42	1 month	11
Automatic hoist rack	5,000	2,950	16	1 1/2 months	27
Hand hoist rack	1,000	1,780	76	?	53
Automatic horizontal barrel	3,500	7,860	13	3 days	31
Automatic horizontal barrel	2,500	11,200	11	3 days	24
Automatic horizontal barrel	2,500	16,200	7	?	24
Automatic horizontal barrel	3,000	3,150	58	?	13
Automatic horizontal barrel	3,200	2,780	6	4 days	31
Hand barrel	2,500	19,200	5	Cut 50%/day; changed every 10 days	10
Hand barrel	3,500	16,000	13	Cut 50%/day; changed every 10 days	41
Hand barrel	3,000	5,600	11	Cut 50% day; changed every 10 days	45

[a] None of the pickle solutions tested contained acid inhibitors.

When significant amounts of dissolved iron are introduced into chloride zinc and alkaline noncyanide zinc-plating baths, rejects are obtained because iron will codeposit on high current density areas, which in turn causes discoloration of the deposit during the chromating process.

Iron forms ferrocyanide and ferricyanide salts almost immediately in a cyanide zinc bath. High concentrations of these salts, along with high sodium carbonate levels, cause various organic additives to become insoluble in the plating bath. This can cause blistering and can produce random spots on the plated parts. But even worse is the fact that these salts are extremely difficult to oxidize during waste treatment, possibly putting the plater out of compliance with government regulations. The dissolved iron (ferrous ion) in chloride zinc baths can readily be treated with oxidizing agents and removed, but this is not usually done until rejects have already occurred. A little-known consequence of precipitating iron from chloride zinc baths is that a significant loss of wetter components can occur. As the proprietary wetter is quite expensive, such losses generate excessive costs to the plater that could be prevented.

What may be surprising to note from Table III is the high concentration of chromium in some of the pickles. Chromium is introduced into the pickle bath by stripping chromated parts, hooks, and danglers. When a great deal of black or yellow chromated parts is run on a line, the chromium level in the pickle is usually on the high side. Chromium contamination can cause blistering, smeary deposits, and skip plate in all types of zinc-plating baths. Skip plate is a term used to describe a lack of deposit in a low current density area of a part.

Copper can be a contaminant in pickle baths but is not studied here because it is a transient type contaminant, that is, it only remains in the pickle solution for a short time and is removed continuously by chemical immersion on the steel parts. Its usual source is brass or brazed parts. The smutty looking black immersion deposit causes blistering of plate that is not related to current density.

ADDING INHIBITORS TO HYDROCHLORIC ACID PICKLE BATHS

As was shown earlier, iron is the major contaminant in pickle solutions. While some of the iron is the result of dissolving rust and scale, a large portion comes from attack by the acid on the base metal. This can be minimized by use of an acid inhibitor. The desired role of an inhibitor is to prevent acid attack on the base metal while allowing the acid to remove rust and scale. It is generally accepted that an inhibitor functions by being attracted to the metal surface and being adsorbed there, preferably on a temporary basis. It is important that the inhibitor not adsorb on the surface of the rust and scale or the acid will not be able to do its cleaning job. Table IV shows how the addition of an acid inhibitor considerably reduces the rate of iron buildup in a pickle. An additional benefit is that hydrogen formation at the surface of the part is reduced, significantly minimizing the chance of hydrogen embrittlement from this source.

All acid inhibitors are not created equal. There are some products offered to the plating industry that simply don't inhibit very well in the hydrochloric acid concentrations that a zinc plater needs to use. There are other products that foam excessively, retard the attack by the acid on scale and rust, or can cause problems in the plating bath such as lowering the cloud point of a chloride zinc bath or forming a film on the parts that is hard to rinse off, causing blistering of plate. Qualities that a good inhibitor should exhibit and provide include:

1. An inhibition rate of ≥95% based on a 24-hr test of carbon steel in 30% hydrochloric acid. (This percentage is derived by comparing the amount by weight of steel dissolved with and without the presence of the inhibitor).
2. No interference with removal of rust and scale.
3. Nonfoaming or produces only a slight amount of unstable foam.

Table IV. Effect of an Acid Inhibitor in a Hydrochloric Acid Pickle Bath for a High-Volume Automatic Hoist Barrel Line [a]

	After 1 Day (ppm)	After 4 Days (ppm)
Dissolved iron in pickle with no inhibitor	7,600	9,310
Dissolved iron in pickle with 1% acid inhibitor[b]	4,080	4,420

[a] Plating bath volume 3,500 gal with 7% drag-out per 22-hr day, plating 14 barrels/hr. Pickle bath volume 550 gal with 42% drag-out per 22-hr day with an average acid concentration of 45%.
[b] Proprietary acid inhibitor manufactured by Columbia Chemical Corp.

4. Compatible with the plating bath following the pickle. (Bath compatibility can be determined by adding the inhibitor directly to a Hull cell with plating bath and plating some test panels. In addition to looking for plating problems, any differences in foaming and cloud point [for chloride zinc baths] should be observed.)
5. Readily rinses off parts and does not produce a hard-to-remove film.
6. Nontoxic and nonflammable for safety of employees.
7. Nonvolatile for longer life in the pickle solution.

WHEN SHOULD A PICKLE SOLUTION BE CHANGED?

Since there are several variables to consider regarding contamination buildup, it is difficult to advise a plater exactly when a pickle bath should be changed. One of the key factors in determining a safe pickle life is the number of rinses and their flow rates between the pickle and the plating bath. This assumes that there are no additional treatment processes before plating. A very simple means of evaluating the efficacy of the rinses prior to plating is to check their average pH. If the last rinse before plating is quite acidic, a significant amount of pickle solution is probably being dragged into the plating tank. If this is the case and it is undesirable for a plater to increase the flow rates of fresh water in the rinses, the pickle life should be monitored very closely.

Another major factor is the rate of drag-out from the pickle tank for a particular plating line. The higher the rate of drag-out, the more closely the pickle should be monitored. The drag-out rate can of course vary somewhat within a given plating line depending on the type of parts being plated. A fairly accurate number for drag-out rates of chloride zinc baths can be calculated by keeping a close track of chloride salt additions needed to maintain a given level of chloride ion. The only way a chloride zinc bath loses chloride ion is through drag-out. Even though the plating bath has somewhat different properties than does the pickle solution, such as surface tension and viscosity, the rates of drag-out of the plating bath and the pickle will be proportional since the equipment, speed of transfer, and part configurations are the same for the two solutions. It is important to note that the volumes of the two tanks are quite different, but the number of racks or barrels exiting from them in a given time is the same. This means that the percent drag-out for a pickle tank is roughly equal to the percent drag-out from the plating tank, multiplied by the ratio of the volumes of the plating tank to the pickle tank. If it is not possible to calculate or estimate the drag-out from a pickle tank, at least a plater should be alert to runs of parts that will drag out more solution than normal and adjust the pickle life accordingly.

The pickle solution in a rack line may build in dissolved iron concentration very slowly, but build in chromium concentration quite rapidly. Just the opposite usually happens in a barrel line. What we recommend is that the plater pick numbers for chromium concentration and iron concentration and see how many working hours it takes to reach these limits. A good starting point for contamination limits is 25 ppm for chromium and 5,000 ppm for iron. When these limits are reached for either element, the pickle should be changed. It is very important that the plater keep track of reject rates and additive consumption to see if improvements have been achieved. Using this as a reference point, the plater can either expand or reduce the working hours for future pickle changes.

CONCLUSION

Zinc platers can save a lot of money and aggravation by paying more attention to the condition of their hydrochloric acid pickle solutions. Acid concentration and contamination levels should be monitored, a safe inhibitor should be used, and rinsing should be optimized whenever possible to avoid pickle contamination of the plating bath.

In the final analysis, a plater must set the guidelines for pickle bath life. Once a history of contamination levels is determined, the best approach is to decide how many working hours should transpire before a pickle bath should be changed. By carefully abiding by this working hour limit, the plater will save considerably by reducing the reject rate as well as reducing the chemical operating costs of the zinc-plating line.

References

1. "Pickling of Iron and Steel," *Metals Handbook, Ninth Edition*, Volume 5, pp. 68–82; American Society for Metals, Metals Park, Ohio; 1982
2. *Metal Finishing Guidebook and Directory Issue*, Elsevier Science Inc., New York; 1994
3. Cook, T.H. et al., *Metal Finishing*, 80(10):15; 1982
4. Pandey, G.N. et al., *Metal Finishing*, 81(4):45; 1983
5. Geduld, H., *Zinc Plating*, ASM International, Metals Park, Ohio; 1988
6. Altmayer, F., *Plating and Surface Finishing*, 78(6):8; 1991

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