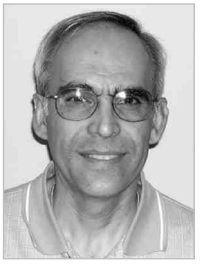

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Additional Procedures & Tips For Analysis & Control: Acid Dips & Pickles

Plating and related process cycles usually include an acidic treatment before the application of critical or main finishes. The acid bath may be required to activate, desmut, remove scale and rust, or any combination of these functions. This step completes the surface cleaning and activation part of the cycle. With good control and effectiveness, the base material should be ready for the main treatment, such as plating or conversion coating. Selecting the right type of acid or its mixture is vital to successful acid treatment. Analysis and maintenance control are major requirements to keep the bath at optimum performance. Let us review some of these critical and important considerations, analysis procedures, and tips.

What Type of Acid

Deciding on what acid solution to use is a function of the base metal (or exposed coating) and targeted or specific treatment. Acids that are effective and suited to some of the common base metals are:

- Steels & Stainless steels. Hydrochloric 5–50% v/v; sulfuric 5–15% v/v; phosphoric 10–20% v/v. Fluorides at 0.25–1 oz/gal help to dissolve carbon smuts and scales. Sometimes mixtures of these acids are used for specific treatments, or the activation of nickel deposits before replating. Wetting agents provide secondary cleaning of oily soils and lower surface tension to aid wetting the surface. This promotes better activity of the acid. Dispersants keep soils from re-depositing on the cleaned surface. Inhibitors prevent over-pickling or etching of the base metal.
- Brass. Sulfuric acid, 3–5% v/v. Most brasses contain some lead, softening the metal for manufacturing steps (extruding, stamping, or forming). Fluorides, at 0.25–0.75 oz/gal, effectively dissolve the lead smuts. Wetting agents provide the cleaning function as described. Inhibitors are sometimes added to minimize the redeposition of copper. Bright dipping, to remove scales and tarnish, is a popular treatment for brasses. Phosphoric/sulfuric acid mixtures have been improved on by the use of hydrogen peroxide/sulfuric acid solutions containing special inhibitors. Also popular are the ferric sulfate/sulfuric acid dips.
- Copper and Alloys. Sulfuric acid, 5–7% v/v. Persulfates at 1–3 oz/gal help to remove scales. Fluorides at 0.2–0.5 oz/gal may also be helpful. Wetting agents provide the cleaning function as described. Inhibitors are sometimes added to minimize the redeposition of copper. Bright dipping, using the newer systems as described in brass, have successfully replaced some nitric acid applications.
- Zinc Castings & Zamak Alloys. 1–2% v/v sulfuric acid with 0.5–0.7% w/v sulfamic acid. Fluorides at 0.3–0.5 oz/gal help to desmut the surface. Wetting agents provide the cleaning function as described.
- White Metal. Solutions and effect similar to description for zinc castings and zamak alloys.

The acid baths may be used at 75–120°F (24-49°C).

Sulfuric is usually the cheapest, and therefore most common pickling acid. Hydrochloric is also a very good pickling agent, however, its fuming properties make it difficult to handle. Many installations prefer the use of hydrochloric acid, because of its quick and effective action in cold solutions. This acid also is well suited to stripping zinc and chrome electrodeposits. Phosphoric acid, a good pickling agent, is somewhat intermediate between sulfuric and hydrochloric acids. Because it forms light iron phosphate coatings on steel, its use is not practical in plating lines. All of the acids described are corrosive and should be handled per the MSDS guidelines. Tanks and ancillary equipment should be selected for appropriate exposure and wear resistance to the corrosive effects of these acids.

Powdered acid mixtures provide equivalent activity to the liquid mineral acids. Additionally, the use of powdered blends offers important safety and handling advantages. These include elimination of fuming concentrates with no rapid heat build-up or dangerous splash-back when making up a new bath or adding to an existing one. Powdered blends are used at 4–32 oz/gal (30–240 g/L).

The majority of metals introduced into a process line exhibit what can be referred to as typical surface conditions. This would include light rust, oxides, and scale. In single and double cleaning cycles, the final acid dip usually is required to only neutralize alkaline films, providing a clean active surface for subsequent finishing. Acid pickles and descaling acids require higher concentrations of the specific acids, with more aggressive treatments (elevated temperatures, longer time, electropickle current densities). Heavier coatings of rust, scale, and oxide, may require off-line

pretreatment, such as sand blasting, mass finishing, electrolytic pickling, electropolishing, hot immersion acid or molten salt bath.

Analysis Control

Baths composed of single mineral acids are easily titrated to a neutralized endpoint, using an appropriate color change indicator (methyl orange, phenolphthalein, etc.). As the bath ages, the solution discoloration or darkening may require the use of direct pH measurement to indicate the titration endpoint. Mixtures of acids require a titration factor based on the initial, fresh working solution make up. For the acid mixture used, ion selective electrodes provide a more quantitative analysis for chlorides and fluorides. Powdered acids are also titrated to a specified endpoint. Additions are made covering all the components of the mixture (*eg*., sulfuric acid, chlorides, fluorides, wetters, deflocculants). Through continued use, the acid bath ages, concentrating in dissolved metals, residual oils, and grease. The titration analysis does not directly provide information or data to track the contamination of the acid, which directly affects the useful service life. Continued maintenance additions will not indefinitely extend bath life. The following tests are quick and helpful to determine bath status and service life.

Specific Gravity Measurement

Measure the bath specific gravity with a hydrometer or by accurately weighing a known volume. Use the value for the newly prepared bath as the set point. The specific gravity will increase as the bath ages. Eventual dumping or replacement of the bath is noted by failure of additions to restore it to preferred activity. The solution specific gravity of the exhausted bath helps to indicate when the useful service life approaches. Appropriate dumping can be scheduled, avoiding costly downtime and unnecessary reject parts.

Dissolved Solids Measurement

Activation and pickling of the base material results in dissolving metals into the acid bath. Depending on the acid titration procedure, the following second step titration may be helpful. After titrating the acid bath to a methyl orange endpoint, add a few drops of phenolphthalein indicator. Continue slowly titrating until the pink endpoint is achieved, or to a pH reading to 7.8. Use the volume of base for the second endpoint as an indicator of the dissolved metals. The point at which the acid bath should be dumped corresponds to the dissolved metals (per volume of the second neutralization titration).

Performance Test—Soak Cleaner

Because you may have already sampled the acid bath for analysis, save a portion of it for an additional, quick performance test. Use a panel of the predominant base metal being processed in the bath (*e.g.*, steel, brass, copper). Clean the panel to confirm absence of water breaks. This test will determine if soils are depositing on the panel (organic, such as oils or copper immersion) or the degree of contamination. It will also indicate if booster adds of the acid are required, in conjunction with the titration analysis.

(1) Using a pair of tongs to avoid physically touching the panel, immerse it in the working acid, maintained at the line operating temperature and time.
(2) Immerse the panel in clean running water for 30 sec.
(3) Inspect the panel for any water breaks (30–60 sec). If water breaks occur, process another fresh panel, to confirm this condition. Otherwise, continue to step #4.
(4) Place the panel at an angle of about 60 degrees and allow water to sheet off the surface. There should be no water breaks. Flash rusting of a steel panel should occur within minutes.

The absence of water breaks will indicate the acid retains sufficient levels of the additive system. Water breaks will confirm an addition of the acid or its mixture is needed. The requirement may coincide with the titration analysis. Make the addition to the acid bath sample and repeat the performance test. Absence of water breaks will confirm the practical need for the addition of acid mixture to the bath on line. If water breaks continue, evaluate the correction by adding up to 25 percent of the initial charge to a new bath. If more than 25 percent is required, the economics may actually justify dumping the bath in favor of a new make-up.

Troubleshooting Tips

- Water breaks. The soak/electrocleaning steps are not removing oils and grease. The acid bath may be weak, requiring corrective addition. Rinsing before the acid is insufficient, because alkaline solution is dragged in, neutralizing the acid.
- Brown film. Weak acid, flash rusting occurs. Electrocleaner weak, causes iron hydroxide film, not fully soluble in the acid. Acid too strong, resulting in flash rust during post rinsing.
- Oil, grease in acid. Insufficient cleaning or rinsing before the acid.
- Rusting after acid. Excessive dissolved metal in acid. Rinsing too long. Transfer time too long.
- Metal smuts in acid. Acid too strong or switch to appropriate acid. ***P&SF***