Finishers' Think Tank



Stephen F. Rudy, CEF Canning Gumm Inc. 538 Forest Street Kearny, NJ 17032 Phone: 201/991-4174 FAX: 201/991-5855

Selecting the Right Acid Treatment

tions, liquid or powder, are available

• Single constituent mineral,

• Combination of two or more

acids; these may consist of

inorganic and organic acids.

· Single or multi-acid combina-

Before making the right choice,

available to us and what they supply.

tures and recommended times will

Some general formulas, bath tempera-

follow the description of the acid bath

This is the simplest type, because the

requirement is not complicated. In

this application, the parts are condi-

tioned as follows: The alkaline film

from the cleaner is neutralized, and

let's identify the acid treatments

tions, which also contain surfac-

tants, dispersants and inhibitors.

in three common forms:

inorganic type.

ur parts have steadily progressed from soak cleaner to electrocleaner. Assuming the cleaning requirements have been met in these process tanks, quality rinsing ensures successful processing so far. A quality finish depends on optimum surface preparation. Approaching this point in the cycle, the parts have been treated in alkaline chemistries. The next step in our "triple play" of cleaning and activation is selecting an appropriate acid treatment. Are we now faced with a new set of choices of what to use and why? You bet! That's the challenge of doing a quality job by making the *right choice*!

Understanding the Process Acid treatment identifies a procedure whereby the base metal is subjected to mild, moderate or aggressive surface etching. It's reasonable to assume the solution pH is below 2.0. What happens chemically can be illustrated by examining the chemical reactions between metal and acid (see box).

The metal as is, before acid bath immersion, contains an

A. Metal oxide + acid = metal salt + waterB. Metal + acid = metal salt + hydrogen (proton)C. Hydrogen (proton) + hydrogen (proton) = hydrogen (gas)

types.

Acid Dip

Acid Treatments

oxide surface layer. This condition has been accentuated by the previous anodic electrocleaning step (oxidation at the anode). This oxide layer hurts our prospective finish two ways: Adhesion of electroplated deposits will be poor and the metal surface in this condition is a poor conductor. The oxide must be totally and cleanly removed. Depending on the degree of surface acid treatment, this can be done in a single immersion, double immersion or perhaps cathodically (in an electrified acid). The acid formulalight oxide and/or rust is attacked and removed, as per our three-set equation above. Many parts fall into this category, which is fine. The simpler, the better. This bath would contain an inorganic acid, typically hydrochloric or sulfuric. It may also include an anionic surfactant to improve wetting of parts by lowering surface tension, removing trace oils and grease and accelerating the activation process. In the case of processing steel, copper and brass together, the acid dip may contain a unique inhibitor, which prevents immersion copper from depositing on steel. Why do I like this option? Because it extends the working life of the acid bath and prevents the nightmare of plated rejects caused by underlying haze and poor adhesion.

When activating brass, the acid typically contains a blend of sulfuric and hydrofluoric acids. Most brass parts have been formed, machined or stamped before being sent to the plater. We can expect, therefore, as much as four percent lead in the alloy, which sufficiently softens the metal. Fluoride is the best additive to dissolve lead smuts, leaving a clean surface before plating.

Copper and copper alloys (beryllium, tellurium, etc.) activate well in formulas containing sulfuric acid and persulfates. This solution provides the right "bite" or etch to deoxidize and desmut.

Most zinc alloys respond well to activation in sulfamic or sulfuric acid blends containing fluorides (preferably ammonium bifluoride). Once again, fluoride effectively dissolves metallic smuts, while the weak inorganic/organic acid mixture promotes activation, but prevents over-pickling. Zinc diecastings are very reactive, highly sensitive to smutting. That's why the acid dip chemistry for zinc is not only important, but must be controlled and applied optimally. The acid formulas just described may also contain surfactants for additional cleaning and surface wetting, deflocculants to prevent redeposition of soils, and inhibitors to eliminate metallic immersion deposits.

Acid Pickle

This process bath is most readily used to condition steel parts. Some metallic smuts and scales do not respond well to the acid dip. What's needed is a more aggressive chemical treatment, readily supplied by the acid pickle. Some heat treat scales, rusts, weld scales and oxides formed by buffing or polishing operations respond well to this bath. The acid pickle will also perform all the functions of the acid dip. A typical acid pickle contains: Sulfuric acid, fluorides and sometimes, chlorides. The aqueous solution forms a powerful stoichiometrically balanced mix of sulfuric, hydrofluoric and hydrochloric acids. The bath can be used electrolytically, combining mechanical and chemical cleaning action. Parts are cathodic. Carbon anodes, especially grades treated to withstand the effect of prolonged fluoride exposure, are recommended. If the electropickle bath contains chloride, generation of corrosive chlorine gas will occur. In some immersion or electrolytic treatments, one can actually see scale peel off in sheets and brown rust spots "whiten," as the chemistry does its job.

In double cleaning cycles, the acid pickle (immersion or cathodic) is usually the first acid step, followed after the second electrocleaner by an acid dip. The first acid may also be chloride-free, to prevent chloride contamination in the second electrocleaner (as discussed in last month's article about electrocleaning).

Descaling Acid

This process bath is a step above the acid pickle with regard to chemical strength and application. Here we refer to removal of heavy deposits: Rusts, scales (hot forging or rolling, casting) and other heat treatments. The bath constituents are similar to the acid pickle, but contain higher levels of accelerators, such as fluorides and chlorides.

Operating parameters—concentration, temperature and time—are usually increased when compared to the acid pickle application. Descaling acids can be used by immersion or electrolytically. These baths are sometimes used to pretreat parts offline before processing in a standard finishing line.

Operating Parameters Acid Dipping				
Application	Sulfuric acid, %v/v	Temp., °F	Time, min	
Steel	5-7	70-90	1-5 (as req.)
Brass & copper	3.5-7	70-90	1-5 (as req.)	
Zinc	1.0-2.0	70-90	1-5 (as req.)
Operating Parameters Steel Treatment Application Sulfuric acid, %v/v Fluoride Chloride Temp., °F Time, min Pickling 6-9 yes optional 75-110 3-5 Descaling 7-12 yes yes 90-160 3-15				
optional cathodic processing: 4-6 volts, 30-50 ASF Nickel Activation-Cathodic Sulfuric acid, %v/v Fluoride Chloride Temp., °F Time, min Volts ASF				
5-11 yes optional 75-120 *1-2 5-7 20-40 *optimum (as required)				
Nickel Activation—Immersion Sulfuric acid, %v/v Iodide, oz/gal Temp., °F Time, min 10-15 2-4 (15-30 gal/L) 75-90 1-5 (as req.)				

Special Needs

Cast Iron

Activation and pickling should be kept to a minimum. Two practical reasons support controlled acid treatment. The low hydrogen overvoltage reduces electroplating efficiency, whereas extended acid immersion further reduces it. Cast irons are quite porous. Strong acids "open" the porosity, sometimes forming heavy smuts, leaving the surface unacceptable for subsequent electroplating. Acids for this application should not contain hydrochloric acid. Rust and scale, when present, should be removed in a mass finishing step or in a reverse current electrocleaner/descaler.

High-carbon

& Case-hardened Steels High-carbon steel can be heavily scaled. Both are susceptible to hydrogen embrittlement. In addition, high-carbon steels generate heavy surface smuts. Sulfuric acid and fluoride blends are preferred to process these metals. In recent years, specially blended pickle aids have been introduced. The concentrates usually contain surfactants, organic acid complexors and inhibitors. They can be added to hydrochloric or sulfuric acid. The acid bath surface tension is reduced, promoting superior surface wetting. Once the scale or smut is removed, an inhibitor film forms to stop additional acid pickling. This prevents hydrogen embrittlement of critical parts, such as spring steel, and repeated smutting of high-carbon steels. In some process cycles, a follow-up electrocleaner is required to remove this inhibitor, followed by an acid dip before plating. Sometimes, the parts can be conditioned in an offline mass-finishing step, before processing in the line using a mild acid dip.

Stainless Steel

Most types respond well to descaling in acid pickles that contain sulfuric acid, chloride and fluoride.

Nickel Activation

There are two effective acid types for activating passive nickel deposits and salvaging reject parts. The immersion bath consists of sulfuric acid and iodide. It promotes an oxidation/ reduction reaction. The nickel deposit contains a surface layer of nickel oxide. Immersion in the bath described causes the nickel oxide to be chemically reduced to nickel metal. This is shown by the following equation:

(Nickel oxide) + (Iodide) = (Nickel metal) + Iodine (elemental) (reduction product) (oxidation product) As this bath ages, the buildup of iodine imparts a deep reddish-brown solution color.

The second nickel activator bath is similar to the previously described acid dip or acid pickle (preferably with chloride included). Reduction of nickel oxide is accomplished by cathodic electropickling and the acidic mixture of components.

Problems & Corrective Measures Water Breaks After the Acid—This is usually the result of poor cleaning or contamination of the acid bath with oils or fatty acids. Correct by improving the cleaning (soak/electrocleaning) or rinsing, as required by careful examination of the problem. Sometimes, oily slicks on the surface or black, greasy rings on the tank walls of the acid bath are observed.

Incomplete Scale or Rust Removal—Select the acid pickle formula for the requirement, modify: Concentration, temperature, time, consider electrolytic pickling.

Rapid Rusting After Acid Treatment—The acid immersion or cathodic pickling may be too aggressive. This problem may also occur during lengthy periods of high relative humidity (dog days of summer).

Parts Smut in the Acid—The acid may be too strong, contain the wrong chemistry or be contaminated.

Poor Reprocessing of Passive Nickel—Insufficient activation in the acid (either by immersion or cathodic). Check bath chemistry, current settings, polarity connections from rectifier to bus, and time. Adjust as required.

Our cycle has now completed the critical portion of surface preparation. After some good rinsing, the parts are clean, active and moving to the plating baths. Having determined what to use, when to use it and how to use it, surface conditions are optimized to get a quality finish. When those parts are ready to enter the soak cleaner, it's really the first big step the most important step.

Next month we'll highlight a metal that needs special treatment for surface preparation. It's that lightweight, but industry heavyweight, metal ... *aluminum*. P&SF

Finishing Trivia

- Aluminum (of course) • There is more aluminum in the
 - Earth's crust than any other metal.Aluminum is never found free. It's always found chemically
 - In 1886, Charles Hall discovered
 - In 1886, Charles Hall discovered a cheap electrolytic process to obtain commercial aluminum.
 - Bauxite and Kaolin are popular ores of aluminum.

Questions for P&SF columnists? Fax to 407/281-6446 or e-mail to editor@aesf.org