Shop Talk: Practical Information for Finishers

Pickling & Acid Dipping

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This is the seventh in a series of reviews looking back on the 25 year-old series, "AES Update," begun by the late Dr. Donald Swalheim, and continued by others. These excerpts remind us how much has gone on before and how relevant it still remains. Though much has changed in the metal finishing industry, a large part of the old stuff is still relevant. As always, I may occasionally add my own words or comments in brackets [ ], just to put things in perspective. The primary goal is to remain faithful to the original article.

This issue, you are looking at an article written by Lawrence J. Durney, on the subject of scale and oxide removal from metals by pickling and acid dipping. The preparatory steps in plating are the ones that are taken for granted, but if we mess up here, the rest of the process might as well be forgotten. As Durney showed, it is critical to do things right the first time ... and at the very beginning.

Pickling

1. Acid + base → H_2O + salt

2. Acid + metal → H_2 + salt

3. Acid + metallic oxide → H_2O + salt

Steel Headlamp Reflector, Before & After Cleaning & Acid Pickling

"On the subject of scale and oxide removal from metals, some platers tend to use **acid pickle** and **acid dip** interchangeably, and frequently refer to a **descaling operation** as a pickle. However, these terms should be distinguished.

"Descaling acids are strong acid dips that remove heat-treating, casting, hot-rolling or forging scales, or heavy rust deposits. Generally, they are not used as part of a plating cycle, but rather as a pretreatment prior to some other finishing step. Unless descaling acids are specially inhibited, they usually remove appreciable amounts of base metal too.

"Acid pickles are moderate-to-strong acid solutions used to remove metallic smuts, light scales such as spot-welding scale or light rust, and to activate the surface by removing oxides generated by polishing and buffing, air oxidation during storage, etc. In addition, acid pickles are used to remove residues such as silicates, which emanate from a foregoing operation such as cleaning.

"Acid dip baths consist of weak-to-moderate acids which are used chiefly to adjust pH before using acid plating solutions. But, they also find utility in the removal of very light rust or oxides that develop as a result of long transfer times in processing.

"Under ideal conditions, every part to be plated is subjected to a specially selected acid step or series of steps in a cycle, with the objective of achieving optimum results. In a practical sense, this is seldom possible and compromise is necessary. Because of the wide variety of substrate materials, shapes, equipment, soils, finishes, etc., the number of potential cycles is almost limitless. For trouble-shooting purposes, however, the acid portions of all the cycles share some common features and problems.

[The essential result, along with typical pickling reactions for plating, is shown in the figure. The first reaction shows the acid neutralizing residual alkaline cleaner. The second and third describe the reactions going on at the metal surface. Ideally, reaction (3) is preferred, with the oxide being removed. However, direct reaction with the metal (2) inevitably occurs at local areas where there is no scale or where scale is removed first. The accompanying table shows the various chemistries used for the more common substrates.]

Troubleshooting Acid Operations

Oil or Tar on Top of Acid

"The cause of oil or tar formation on top of acid solutions almost always occurs before the part reaches the acid step. Check for incomplete cleaning and dragged-in soap from a previous cleaner. Remember that some soaps will set if the rinsewater is too cold, and it follows that warming the rinse after the cleaner may get rid of the problem. The oil and tar may sometimes be eliminated by using wetting agents, but this is a crutch and should be used only as a temporary expedient.

Rusting During Transfer Or During Rinse

"Too long a transfer time, too weak an acid, too much time for post rinsing, or too much dissolved metal in the acid solutions are the usual causes of rusting during transfers through the rinsing stage. It is sometimes helpful to reduce the flow of water in the rinse, converting it into a weak acid dip which either removes rust or prevents its formation. Strengthening the acid or making a new acid solution usually corrects the problem if it is due to other causes.

Smut Formation in Acid Dip

“If the acid is too strong for the alloy being processed or if the acid is contaminated with some other metal, smut will form on the alloy surfaces. Determining which of these is the cause requires some careful testing, but the addition of an inhibitor will sometimes correct either one or both of the conditions. Inhibitors, which come in liquid and solid forms, reduce attack of the metal substrate areas where scale is removed first. They function by forming adsorbed films on the clean metal surface. Inhibitors are particularly effective if the contaminating metal is copper.

Smut Formation in the Rinse

“A common occurrence with steel when brass or copper is processed on the same line is smut formation during the rinsing stage. Copper dissolved from racks causes smut formation on steel; this also frequently happens with aluminum alloys when copper from racks or parts being processed dissolves in the acid. The acid is strong enough to hold metal in solution until it is diluted by rinsewater, which precipitates copper [as a] smut. Eventually, however, a significant increase in the contamination level will lead to smut formation on parts during immersion in the acid tank.

“To correct the situation when steel and brass are being used on the same line, use an inhibitor in the acid. When copper contamination from racks is a problem, strip the racks every cycle and use an inhibitor in the acid. Rectifying smut formation when processing aluminum calls for the use of titanium or stainless [steel] racks and stripping at every cycle. Other good corrective measures for smut problems with aluminum are: dumping acid more frequently or adding a weak nitric-acid step to remove the deposit. [A chromate-type desmutter was also suggested, but today’s trend away from hexavalent chromium chemistry may preclude its use.]

Acid Solutions for Some Metal Substrates

Metal Substrate	**Common Acid Solutions**[1]
Aluminum	25–50 v/o nitric acid
Copper, copper alloys	5–15 v/o sulfuric or hydrochloric acid
High-carbon steel	Anodic treatment in 20–65 v/o sulfuric acid, 150–400 ASF, 1 min
Leaded bronze	5–25 v/o fluoboric acid
Stainless steels	1–2 v/o sulfuric and 0.1 v/o hydrofluoric acids, 1–2 min
Steel	5–10 v/o sulfuric acid, 15 sec to 2 min[2]
Zinc die castings	0.25–0.75 v/o sulfuric acid, 20–30 sec

[1] All solutions at room temperature.

[2] A 3–6 v/o sulfuric acid solution heated to 70–80°C (158–176°F) is commonly used for removing heavy scale.

Water Break After Acid Dip

“Often a difficult problem to track down, water-breaking after acid dipping requires very careful observation to determine exactly which of the causes exists. Once pinpointed, however, the solution is usually simple. The causes are inadequate cleaning, acid contaminated with oil or fatty acid from soap, acid containing incompatible wetting agents and/or inhibitors, or oils held under metallic smuts on surfaces.

“Common causes for the inability of an acid solution to remove light scale or oxide film include the use of too-weak an acid and the necessity for an addition of activators such as a fluoride salt into the acid. It is important to find out if the acid had been working properly prior to the identification of the problem, and if parts and/or scales are the same as existed on previously processed parts.

“Spot-welding scale, in particular, frequently vary in their difficulty of removal depending on the condition of the wire as it goes to the spot-welder (wire source, lubricant, etc. - have they been changed?); the conditions of welding (voltages, amperages, dwell-time, etc. - have they been altered?); and the storage conditions after welding and before plating.

Types of Smut

“There are two basic types of smut: non-conductive and conductive.

Non-Conductive Smut

“Non-conductive smut usually consists of inorganic particles which may be dirt, abrasives from buffing compounds, carbon, silicon or other alloying constituents brought to the surface during an etching or severe pickling operation, or a carbon deposit left from heat-treating, brazing, gas-welding, etc.

“Usually, reverse-current cleaning eliminates non-conductive smuts, although, in difficult cases, it may be necessary to use high currents and/or heavily chelated materials. Chelates also are usually good deflocculants and help to remove smut, both by deflocculating or suspending it in solution, and, perhaps, by dissolving a small amount of the metal substrate, thus helping to remove smut from the surface. In some cases, it may even be necessary to use an alkaline deruster type of material, possibly even with periodic-reverse current.

Conductive Smut

“Conductive smuts, which are usually metallic, may consist of fine particles from buffing or polishing operations. They may also occur as a result of machining, drawing or stamping operations. Metallic fines are a nuisance because they are often strongly attracted to surfaces and may adhere sufficiently to interfere with oil removal in a contact area. Sometimes, these fine-particle smuts arise from metal precipitation from contaminated acid solutions.

“Conductive smuts, with the exception of those resulting from contamination of the acid, usually do not respond to reverse-current cleaning or, for that matter, even to direct-current cleaning. Since they are metallic, conductive smuts are best erased by strong acids. Metallic smuts on steel, for example, may require hydrochloric acid as strong as 75 percent by volume. As mentioned, these metallic smuts may adhere so strongly to the surface that they prevent complete oil removal, which allows the oil to show up after the smut is removed. If this happens, a subsequent alkaline cleaning step may be necessary.

Cathodic Pickling

"How about cathodic pickling? Electrolytic pickling has been used for many years, yet no common consensus has been expressed on how well it works. For some people, it has been a tremendous help; others have found the results so erratic that they question the wisdom of using current in pickling operations. The problems generally stem from:

- **Changes in one or more of the bath constituents as a result of oxidation at the anode** Some wetting agents, for example, may oxidize to become poorly soluble oils that rinse very slowly and leave a haze; or
- **Contaminants that may actually start to plate out.** Because, in most cases, electrolytic pickles use direct current, the conditions are ripe for an unwanted plating operation. For example, iron from the inside of tubing can build up to a point in which it will plate out in the high-current-density areas; or
- **Dragged-in materials from other pre-cleaning steps that may undergo reactions leading to problems with an otherwise acceptable acid.** The wrong wetter in a cleaner may be dragged into the electrolytic pickle and cause problems in the pickle by oxidizing; or
- **Carbon anodes that break up.** However, if lead anodes are used, the lead may become the contaminant that is unintentionally plated out.

"It is safe to say that nobody can avoid all cathodic-pickle problems, but there are some guidelines which can make the job a lot easier. One recommendation is to use only the simpler powdered acids, whenever possible. These acids, which do not contain fluorides or other accelerators, permit the use of lead anodes instead of carbon anodes, which are more likely to break up. Only occasionally will enough lead dissolve to cause a plating-out problem. When using lead anodes, it is a good idea to avoid excessive anode current densities.

"A second guideline is to watch for iron build-up if there are appreciable blind areas with articles such as tubing, and to change the solution before trouble develops. Inhibited acids facilitate the operation.

"If fluoride-type acids must be used, circumvent any problems as much as possible by using the best-grade carbon anodes available, while keeping the current density low and skimming the surface of the tank often.

"Make sure that cleaners used before the electrolytic pickle have compatible wetting agents. Use the cleaner that does an effective job with the least amount of wetter possible.

"After the cathodic pickle treatment, ensure good rinsing of the article, paying careful attention to this phase of the operation.

"Finally, a reverse-current electrocleaner following the electrolytic pickling operation should be employed if at all possible. This should be followed by a rinse and a dilute acid dip if the plating solution is an acid solution. Admittedly, this procedure makes for a rather long cycle, but many of the older plating machines have room for these steps and it certainly helps to produce a better final piece of work." P&SF