PICKLING AND ACID DIPPING

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Metals can be immersed into solutions of acids to remove metal, metal oxides, heat treat scale and foreign metals. Such treatments generally leave the surface chemically clean and ready for further processing.

The general process is to solvent, emulsion or alkaline clean the parts prior to acid immersion, so the acid solutions will wet and/or etch uniformly. The part should be free of water breaks after the alkaline step and should remain so throughout processing.

Parts should be racked so that:

1. They can be completely immersed in the pickling solution to avoid an air/solution interface where preferential etching can occur.
2. They do not strike or touch each other.
3. There is free draining and rinse water can contact all surfaces.
4. There are no solution pockets which prevent complete solution contact, but provide a solution/air interface.

Assemblies containing overlapping surfaces, such as riveted joints, and assemblies containing more than one metal, such as an aluminum assembly with cadmium or stainless steel inserts, should be avoided.

Pickling of two alloys of the same material at one time should be checked to ascertain that galvanic effects will not cause preferential etching of one of the alloys.

ALUMINUM AND ALUMINUM ALLOYS

Pickling:

Mild acid etching of wrought materials to remove heavy oxides, corrosion products and heat treat discoloration, can be accomplished by immersion in various combinations of sulfuric, nitric, hydrofluoric and chromic acids. The following solutions are typical:

	Make up	*Maintenance*
Nitric acid	25% v	25-30 oz/gal
Hydrofluoric acid	1% v	To maintain etch rate
Temperature		Room
Etch rate		0.0015-0.003 inch/side/hr

Maintenance of etch rate can be accomplished by addition of hydrofluoric acid or ammonium bifluoride.

	Make up	*Maintenance*
Sodium dichromate	7.5 oz/gal	Cr^{+6} 2.0-3.0 oz/gal
Sulfuric acid	10% v	20-27 oz/gal H_2SO_4
Ammonium bifluoride	1.75 oz/gal	To maintain etch rate
Etch rate		0.0003-0.0004 inch/side/hr
Temperature		Room

Hydrofluoric acid can be added to maintain etch rate; 2.5 fluid oz of HF is equal to 1 oz ammonium bifluoride. The etch rate of this solution can be increased to 0.001 inch/side/hour by substituting 10% nitric acid for the sulfuric acid. The etch rate is still controlled by the fluoride.

Heavy metal removal and brightening of both wrought materials and castings may be accomplished by immersion into a solution of:

to add corrosion resistance to the cadmium it, also, may be painted. Both of these coatings are usually applied from proprietary baths, but immersion in these solutions will give a sufficient passivated surface for painting.

Chromate Solution:

Sodium dichromate	10 oz/gal
Sulfuric acid	10 oz/gal

Phosphate Solution:

Phosphoric acid	10 oz/gal
Zinc phosphate	3 oz/gal

CHROMIUM

A fine sandblasting with one of the hard abrasives, aluminum oxide or silicon carbide, to remove the gloss or smooth surface followed by priming as soon as possible will develop a satisfactory adhesion.

COPPER

Conversion coatings on copper prior to painting are usually not necessary, however, copper which is primed prior to adhesive bonding is usually treated in a mild acid oxidizing solution prior to primer.

After cleaning, a mild abrasive treatment followed by the primer is sufficient to paint copper. Since corrosion resistance is usually not a reason to paint copper, the primer can be the so-called "wash-primer".

IRON AND STEEL

Iron and steel products which are rusted or covered with heat treat scale need to be cleaned prior to painting. The usual ways of doing this are to pickle the steel to remove the rust or to mechanically remove the rust. Pickling can be accomplished as indicated in the pickling section using hydrochloric or sulfuric acid. If smut is found, it must be removed following the usual procedures (sandblasting is satisfactory). Both of these operations should be followed immediately by priming with a good anticorrosive primer.

Heat treat scale (blue scale) which is firm and uniform does not necessarily need to be removed from steel prior to painting. If it is not removed, however, the parts may suffer more severe pitting or oxygen cell type corrosion where there is a break down in the primer coating in service.

Steel which cannot be primed immediately should be phosphate coated. The light zinc phosphate meeting TT-C-490, type I or DOD-P-16232, type Z are recommended (See "Phosphate Coatings"). The time delay between phosphating and painting can be as required, but it is best to keep the parts as clean as possible since it is difficult to get oil off the crystalline surface of the phosphate.

LEAD

The cleaned lead can be coated with "wash-primer" followed by the topcoat for satisfactory adhesion.

MAGNESIUM

Magnesium must be treated with a conversion coating or anodized before painting. Products to be used in mild environments and not mechanically abused can be given a

Sodium/potassium hydroxide	2-10 oz/gal
Temperature	Room-180°F
Time	To desired etching

The etch rate depends on the concentration of the solution and the temperature. Higher temperatures and low concentrations are desirable.

The smut which forms on wrought materials of 2000, 7000 and sometimes 6000 series alloys can be removed by immersion in the nitric/hydrofluoric solution above. The smut or black to brown film formed on castings can be removed by dipping in a concentrated nitric acid solution containing some fluoride.

Nitric acid	75% v
Hydrofluoric acid	25% v
Temperature	Room
Time	1-2 min for sand castings
	15-30 sec for others

This solution may be used to treat castings whether they have been etched or not and is an excellent method of opening porosity prior to sealing operations.

Removal of foreign metals from aluminum parts, especially lead from parts formed on lead or kirtsite dies, may be accomplished in the following solution:

	Make up	*Maintenance*
Nitric acid	25% v	20-35 oz/gal
Sodium dichromate	3.25 oz/gal	2.5-4.0 "
Molybdic acid	0.5 "	0.3-0.6 "
Temperature		120-150°F
Time of immersion		5-10 min

Bright Dipping:

The following solutions will remove oxides and corrosion products without etching the aluminum:

	Make Up	*Maintenance*
1. Tragacanth gum	0.5-1 oz/gal	—
Hydrofluoric acid	4.5-5% v	4-6 oz/gal as HF by analysis
Temperature		Room

Add the gum tragacanth to denatured ethyl alcohol to make a thin paste. Add the paste to the tank filled with water heated to 180 to 212°F. Cool the tank to room temperature then add the acid.

	Make Up	*Maintenance*
2. Hydrofluosilic acid	4% v	1.2-1.6 oz/gal as H_2SiF_6 by analysis
Wetting agent (Nacconol)	0.1 oz/gal	0.1-0.06 oz/gal
Temperature		Room

	Make Up	*Maintenance*
3. Phosphoric acid	80% v	
Nitric acid	5% v	Dump when no longer effective
Acetic acid	5% v	
Water	Remainder	
Temperature		To 220°F

GOLD AND GOLD ALLOYS

Gold alloys can be brightened by anodic treatment at 6 to 12 V in solutions in which gold is soluble. The following solutions are examples:

	Make Up	*Maintenance*
1. Potassium cyanide	8 oz/gal	4-8 oz/gal
Rochelle salts	4 "	3.4 "
or		
Potassium ferrocyanide	2 "	1.5-2 "
Temperature		150-175 °F
2. Sodium cyanide	8 "	6-8 oz/gal
Disodium phosphate	2 "	1-2 "
Temperature		150-170 °F

Gold can be recovered from the baths by low current electrolizing onto stainless steel cathodes with stainless steel anodes.

IRON AND STEEL

The usual solutions for the removal of scale and rust from iron and steel products are hydrochloric or sulfuric acids. These are used in concentration ranges from a few ounces per gallon to very concentrated, depending on the type of work being processed. Cold rolled steel can be pickled rapidly in weak hydrochloric acid, while heavily scaled construction plate is best pickled in concentrated sulfuric.

Commercial inhibitors, amines and nitrates are common and are optionally used in these pickles to prevent overetching and to avoid pitting. Satisfactory formulas include:

	Make Up	*Maintenance*
1. Hydrochloric acid		
(20° Baumé)	55% v	23-40 oz/gal
Inhibitor (optional)		As required
Temperature		Room
Time		0.5-5 min
Iron		Up to 5 oz/gal
Copper		0.5 oz/gal max
2. Sulfuric acid		
(66° Baumé)	25% v	50-65 oz/gal
Inhibitor (optional)		As required
Temperature		Room to 120 °F
Time		Up to 10 min

Solution may be used with lead-lined tanks and lead heating coils.

Alloy Steel, 400 Series and pH Hardened Steels:

These steels may be pickled in hydrochloric acid solutions (See 1 above), for one to 10 minutes for heavy scales, and no more than five minutes for light scales.

Other solutions particularly suited to the 400 series and PH steels are as follows:

	Make Up	*Maintenance*
3. Ferric sulfate anhydrous	13.5 oz/gal	8.5-13.5 oz/gal
Hydrofluoric acid (70%)	1.7% v	1.5-2.5 "
Temperature		125-135°F
Time		1-5 min
4. Sodium chloride	4 oz/gal	2-4 oz/gal
Sulfuric acid (66° Baumé)	10% v	17-27 "
Temperature		160-180°F
Time		1-5 min
5. Sulfuric acid (66° Baumé)	1% v	2-3 oz/gal
Potassium nitrate	3 oz/gal	2-3 "
Temperature		160°F
Time		5-15 min
6. Potassium permanganate	12 oz/gal	8-12 oz/gal
Sodium hydroxide	12 "	8-12 "
Temperature		160°F to boiling
Time		Up to 30 min

Solution 6 is used to loosen heavy scale and should be followed by pickling in solutions 1 or 2 above.

Molten Salt Descaling:

Molten salt baths are available for descaling steel and stainless steels. They are proprietary and operate in the temperature range of 400 to 1000°F. They do not attack the base metals and are particularly useful where heavy scales must be removed and acid

solutions sometimes attack the basis metal in preference to the scale leaving it etched and pitted.

Cast Irons:

Cast irons can be pickled in solutions which combine sulfuric acid with other acids.

	Make Up	*Maintenance*
7. Sulfuric acid (66° Baumé)	5-10% v	10-15 oz/gal
		or
		25-30 "
Nitric acid (40° Baumé)	5% v	4-5 "
or		
Hydrofluoric acid (70%)	10% v	12-15 "

Bright Dips:

Bright dipping of steel is not generally satisfactory. For brightening, electropolishing at high current densities is recommended.

Solutions containing citric acid (10 to 12 oz/gal), to which ammonia is added to produce a pH of 6.5 to 7 and used at boiling, will brighten cold rolled steel without removing metal. Oxalic acid at 1 to 2 oz/gal and hydrogen peroxide (100% v) at 0.5 oz/gal mixed in solution with a trace of sulfate will also act as a brightener.

MAGNESIUM ALLOYS

Pickling:

Removal of mill scale, corrosion and heavy oxides may be accomplished in the following solutions:

	Make Up	*Maintenance*
1. Hydrofluoric acid	23% v	24-29 oz/gal as HF
Temperature		Room

Solution should be water-clear before parts are processed — allow sludge to settle.

	Make Up	*Maintenance*
2. Chromic acid	40 oz/gal	32-40 oz/gal
Nitric acid (40° Baumé)	2.5% v	2-3.5 "
Ammonium bifluoride	0.25 oz/gal	0.03 to 0.25 oz/gal

Control by draw off and replacement when parts are left stained after rinsing in cold water.

Removal of surface contamination and pickling of parts with minimum dimensional change may be accomplished in the following solutions:

	Make Up	*Maintenance*
3. Chromic acid	48 oz/gal	44-48 oz/gal
Sodium nitrate	4 "	3.5-4 "
Chlorides		0.01 oz/gal max as Cl
Sulfate		0.05 oz/gal max as SO_4
pH		0.7
Temperature		65-90°F
Etch rate		20-30 microinch/side/min