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:

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

CADMIUM

Pickling:

To remove heat discoloration from cadmium, 1% solutions of sulfuric acid or nitric acid will be found effective. Immersion in these solutions will activate the parts prior to chromate conversion treatment. Use the acid which is common with the conversion coating without rinsing between steps.

Bright Dipping:

The following solutions may be used:

	Make Up	*Maintenance*
1. Chromic acid	15 oz/gal	12-15 oz/gal
Sulfuric acid	0.5 fl oz/gal	—
Temperature		Room
2. Nitric acid	1% v	—
Temperature		Room
3. Sulfuric acid	1% v	—
Temperature		Room

COBALT (SEE NICKEL)

Pickling:

The removal of scales from copper alloys can be accomplished in solutions of sulfuric acid and where the scales are heavy by adding an oxidizing acid. The following solutions are examples:

1. To remove heavy scale (red or fire scale):

	Make Up	*Maintenance*
Sulfuric acid (66° Baumé)	32% v	55-80 oz/gal
Nitric acid (40° Baumé)	12% v	10-15 "
Temperature		Room
Copper		3 oz/gal max

2. For moderate scales:

	Make Up	*Maintenance*
Sulfuric acid (66° Baumé)	12% v	20-30 oz/gal
Chromic acid	4 oz/gal	3-4 "
or		
Sodium dichromate	6 "	4.5-6 "
Temperature		Room
Copper		2.0 oz/gal max

3. For light scales:

	Make Up	*Maintenance*
Sulfuric acid (66° Baumé)	10% v	19-26 oz/gal
Temperature		Room to 125°F
Copper		Up to 4 oz/gal

Alloys which contain more than 0.7% lead can be treated in a fluoboric acid solution, either as a supplementary treatment to remove smut after pickling in the above solutions or as an oxide (tarnish) remover prior to plating:

	Make Up	*Maintenance*
4. Fluoboric acid (49%)	25% v	15-24 oz/gal
Temperature		Room
Copper		1.5 oz/gal max

By adding up to 5% hydrogen peroxide, the bath may be used to remove excess solder from parts prior to mechanical treatment.

Copper clad laminants to be used for circuit boards may be pickled in the following solutions:

	Make Up	*Maintenance*
5. Ammonium persulfate	32% v	—
Temperature		Room to 100°F max
Etch rate	Discard the solution when the rate drops below 30 microinches/min	

	Make Up	*Maintenance*
6. Nitric acid (40° Baumé)	30% v	30-36 oz/gal
Phosphoric acid (75%)	15% v	20-25 "
Temperature		Room to 100°F max
Copper		1.5 oz/gal max

Bright Dipping:

Solutions 4, 5, and 6 will act as effective bright dips, however, the following solutions may be considered:

	Make Up	*Maintenance*
1. Sulfuric acid (66° Baumé)	44% v	90-110 oz/gal
Nitric acid (40° Baumé)	22% v	20-25 "
Water	33% v	—
Sodium chloride	0.25 oz/gal	

The chloride adds luster to copper; however, excess can cause spotting.

	Make Up	*Maintenance*
2. Phosphoric acid (85%)	55% v	
Nitric acid (40° Baumé)	20% v	
Acetic acid (98%)	25% v	
Temperature		130-175°F

Discard when the solution absorbs water and becomes an etching solution.

	Make Up	*Maintenance*
3. Sodium cyanide	6 oz/gal	4-6 oz/gal
Temperature		120-150°F

Solution may be used at a lower temperature with current applied anodically to the part to effectively act as a brightener.

This solution may also be used to dip acid pickled or bright dipped parts to prevent tarnish until further treatment is accomplished.

Mat Finishing:

Copper alloys may be etched in the following solutions to provide a mat or dull finish.

	Make Up	*Maintenance*
1. Hydrochloric acid	50% v	Discard when ineffective
Ferric chloride (40° Baumé)	50% v	
Temperature		Room

After etching and rinsing, parts may need a bright dip to remove the smut which forms on some alloys.

	Make Up	*Maintenance*
2. Sulfuric acid (66° Baumé)	5% v	10-13 oz/gal
Ferric sulfate	13 oz/gal	10-13 "
Temperature		up to 140°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

Small quantities of fluorides, chlorides and sulfates alone or in any combination activate the solution. Increasing the ions increases etch rate and increasing chlorides may cause pitting.

	Make Up	*Maintenance*
4. Chromic acid	24 oz/gal	21-27 oz/gal
Sulfuric acid	0.3% v	0.07-0.08 oz/gal as H_2SO_4 by analysis
Trivalent chromium		2 oz/gal as Cr_2O_3
Temperature		Room

Maintain by draw off to prevent aged solution from staining parts.

	Make Up	*Maintenance*
5. Phosphoric acid (85%)	Full strength	—

	Make Up	*Maintenance*
6. Chromic acid	24 oz/gal	23-25 oz/gal
Temperature		Room to 100°F
		or
		190-212°F
Etch rate		300 microinch/side/hr

The following solution works well as a hand treatment:

	Make Up	*Maintenance*
7. Sodium dichromate	24 oz/gal	—
Nitric acid (40° Baumé)	22% v	—
Temperature		Room

Dispense the amount needed from the polyethylene storage bottle. Discard solution after use.

NICKEL AND COBALT ALLOYS

Many of the baths used to pickle stainless steels will also work for these alloys.

The permanganate scale loosening bath given under iron and steel, Solution 6, can be used to treat parts with heavy scale. A 30-minute soak will loosen the scale so that it can be removed in any of the following baths or the nitric/hydrofluoric baths under stainless steels.

For alloys covered by AISI 661, 670, 680, 688:

	Make Up	*Maintenance*
1. Hydrofluoric (70%)	50% v	48-58 oz/gal
Nitric acid (40° Baumé)	7.5% v	7-10 "
Temperature		Room

	Make Up	*Maintenance*
2. Sodium hydride	1-2% wt	—
Sodium hydroxide	98-99% wt	—
Temperature		680-720°F

Parts treated in the molten bath which develop scale, and pure nickel or monel parts, may be treated in hydrochloric acid.

	Make Up	*Maintenance*
3. Hydrochloric acid (22° Baumé)	50-75% v	—
Temperature		Room

Parts with light scales and discoloration can be treated in the following solutions. Nickel silver (German silver) can also be treated in Solution 4.

	Make Up	*Maintenance*
4. Sulfuric acid (66° Baumé)	5% v	10-15 oz/gal
Ferric sulfate (anhydrous)	24 oz/gal	22-24 "
Temperature		180°F
5. Hydrochloric acid (22° Baumé)	25% v	10-13 oz/gal
Ferric sulfate (anhydrous)	13 oz/gal	10-13 "
Temperature		160-180°F

SILVER

Silver and silver alloys can be treated in strong acids and in cyanide solutions typical of the following:

	Make Up	*Maintenance*
1. Nitric acid (40° Baumé)	66% v	—
Temperature		Room to 160°F

	Make Up	*Maintenance*
2. Sulfuric acid (66° Baumé)	88% v	—
Nitric acid (40° Baumé)	22% v	—
Temperature		Room

Work must be dry when immersing, or spotting will occur.

	Make Up	*Maintenance*
3. Sodium cyanide	4 oz/gal	3-4 oz/gal
Sodium carbonate	2 "	1-2 "
Sodium aluminum sulfate	6 "	—
or		
Sodium potassium tartrate	6 "	—
Temperature		180-210°F

Solution may be used with 4 to 6 V cathodic current for very short periods of time (30 sec to one min). With current, the solution may be used at room temperature.

STAINLESS STEELS

Stainless steels can be pickled in a variety of acid solutions including hydrochloric acid. Since, however, hydrochloric acid can cause intergranular attack and residual chloride ions may cause stress corrosion during service of the part, it is not recommended as a pickle solution.

The scales which form on stainless steels are sometimes resistant to acid treatments

and attempts to remove them with acids can cause pitting and etching of the substrate. It is recommended that such scale be loosened in scale conditioning prior to pickling.

Scale Loosening:

	Make Up	*Maintenance*
1. Sodium hydroxide	25 oz/gal	20-25 oz/gal as Na_2O
Sodium carbonate (anhydrous)	25 "	
Potassium permanganate	8 "	6-8 oz/gal
Temperature		190°F to boiling

	Make Up	*Maintenance*
2. Sodium carbonate (anhydrous)	20 oz/gal	7-9 oz/gal as Na_2O
Sodium hydroxide	5 "	
Potassium permanganate	12 "	10-12 oz/gal
Temperature		190°F to boiling

	Make Up	*Maintenance*
3. Sodium carbonate (anhydrous)	12 oz/gal	10-12 oz/gal
Potassium permanganate	12 "	10-12 "
Temperature		190°F to boiling

	Make Up	*Maintenance*
4. Sulfuric acid (66° Baumé)	10% v	—
Temperature		180°F

Pickling:

	Make Up	*Maintenance*
5. Nitric acid (40° Baumé)	30% v	30-65 oz/gal
Hydrofluoric acid (70%)	4% v	To maintain etch rate
or		
Ammonium bifluoride	6.7 oz/gal	
Etch rate		0.001 to 0.003 inch/side/hr
Dissolved metal		3 oz/gal max of Fe
Temperature		120-140°F

Immerse for five-minute intervals for a total of 30 minutes. Further processing may cause etching.

Many variations of this bath exist with both higher and lower acid concentrations and with wetting agents. Lower fluoride slows etch rate; higher nitric acid allows the bath to function at lower temperatures. Any of these solutions may etch cold worked areas of parts, so they should be used with caution.

	Make Up	*Maintenance*
6. Sulfuric acid (66° Baumé)	6.25% v	—
Hydrofluoric acid (75%)	6.25% v	—
Chromic acid	8 oz/gal	—
Temperature		to 180°F

	Make Up	Maintenance
7. Ferric sulfate	13 oz/gal	9-13 oz/gal
Hydrofluoric acid (75%)	1.7% v	1.5-2.5 as fluoride
Temperature		125-135°F

	Make Up	Maintenance
8. Sulfamic acid	10 oz/gal	—
Ferric sulfate	0.25 "	
Temperature		160-180°F

	Make Up	Maintenance
9. Nitric acid (40° Baumé)	40% v	45-70 oz/gal
Molybdic acid	0.5 oz/gal	0.3-0.5 "

This solution will remove foreign metals, especially lead, and will leave the part passive.

Passivation:

	Make Up	Maintenance
10. Nitric acid (40° Baumé)	40% v	45-70 oz/gal
Temperature		Room to 145°F

	Make Up	Maintenance
11. Nitric acid (40° Baumé)	25% v	20-35 oz/gal
Sodium dichromate	4 oz/gal	2.5-4 "
Temperature		70-150°F

	Make Up	Maintenance
12. Sodium dichromate	8 oz/gal	6-8 oz/gal
Temperature		140-160°F
Time		Up to 30 min

This solution can be used to passivate after any of the above pickles.

STEEL (SEE IRON AND STEEL)

TITANIUM

Solution 5 under stainless steels can be used; however, the following bath is preferred because the higher nitric acid content gives better assurance of avoiding hydrogen embrittlement.

	Make Up	Maintenance
1. Nitric acid (40° Baumé)	40% v	40-60 oz/gal
Hydrofluoric acid (75%)	2.4% v	To maintain etch rate
or		
Ammonium bifluoride	4 oz/gal	
Dissolved metals		4 oz/gal of Ti
when also used for CRES		3 oz/gal of Fe
Temperature		120-135°F

May be used with a wetting agent to lower surface tension and give better wetting.

	Make Up	Maintenance
2. Fused sodium hydroxide	100% wt	—
Temperature		800°F

The permanganate scale looseners, Solutions 1 and 2 under stainless steels, may be used followed by pickling in Solution 1 above.

ZINC AND ZINC ALLOYS

Zinc can be activated by immersion in 1% v solutions of sulfuric or hydrochloric acids. For bright finishes, these should be used with chromic acid.

	Make Up	Maintenance
1. Chromic acid	40 oz/gal	30-40 oz/gal
Sodium sulfate	4 "	2-4 "
Temperature		Room
Time		5-30 sec

This is followed, after a rinse, by immersion in a 1% sulfuric acid bath if a yellow film has formed.

	Make Up	Maintenance
2. Chromic acid	40 oz/gal	30-40 oz/gal
Hydrochloric acid	12 fl oz/gal	—
Temperature		Room
Time		1 min

This is followed after a rinse by immersion in chromic acid solution of 40 oz/gal.

ZIRCONIUM

Zirconium with heavy scale should be treated in a scale conditioning bath, such as the permanganate Solutions 1 and 2 under stainless steel. This is followed by short immersion in a nitric hydrofluoric bath such as Solution 5 under stainless steels or the following:

	Make Up	Maintenance
Nitric acid (40° Baumé)	47% v	50-60 oz/gal
Hydrofluoric acid (75%)	5% v	2-5 "
Temperature		Room

Excessive fluorides will etch the metal. If etching occurs, reduce total fluoride.