Surface Preparation of Various Metal Alloys Before Plating

Stephen F. Rudy, CEF, Enequist Chemical, Brooklyn, NY

The first step in any finishing process is the most important. Most metal alloys follow a standard progression of soak cleaning, electrocleaning and acid activiation/pickling before application of electroplated or electroless topcoats. There are, however, special considerations regarding types of chemistries to use in the process baths: What to use, when to use and how to use. This paper stresses the importance of identifying the base metal (alloy and surface characteristics), types of soil removed, chemistry requirements, cleaning mechanism and operating limitations. Special consideration is given to aluminum, which requires unique processing. The benefits of mass finishing and spray cleaning to help condition surfaces in off-line ptretreatment will also be addressed.

For more information, contact:
Stephen F. Rudy, CEF
Enequist Chemical Co.
100 Varick Ave.
Brooklyn, NY 11237
Phone 718/497-1200
e-mail: sfrudy@aol.com

Surface Preparation of Various Metal Alloys Before Plating

by
Stephen F. Rudy
Enequist Chemical Company

This paper will focus on practical information related to chemical process bath selection to condition several metals and alloys before electroplating. An important fact to be highlighted is the critical contribution of surface preparation to a satisfactory plated finish. This includes cleaning, rinsing, and activation. *Metal finishing process cycles predominantly begin with these initial steps.* In essence, the first step is the most important step. If the surface preparation portion of the cycle is not correct, the effective application of any plated deposit may result in blisters, hazing, pitting, lack of adhesion, or other related finish failures. This problem hurts the finisher several ways, such as: finished parts may be only marginally acceptable, costly rejects, failure to meet production quota, potential to shut down the line. Therefore it's important to map out an effective strategy and game plan. Some key items to acknowledge are:

- Keep It Clean — Do It Right
- Keep it Active — Do It Now
- Keep It Moving — Do It Once

There are three basic considerations for selecting the right cleaning and activation solutions: what to use, when to use, and how to use. These general questions are supported by specific guidelines to help us make the right choices:

- Identify the Base Metal
(type, alloy, surface characteristics)

- Limitations
(process line, chemistry, temperature, time)

- Rinsing Characteristics
(parts, equipment, process line)

The next set of considerations address the concern for sufficient, complete soil removal. The condition of the parts, (i.e. soils and existing surface coatings):

- Types of Soils
(oils, grease, shop dirt, buffing & polishing cmpds, smuts, scales)

- Existing Finishes
(phosphates, electroplated coatings, chromates, rust inhibitors)

How do we gain the initiative in process selection without getting confused or out of focus? The easiest way is to segregate each process tank in decision making, using the following example:

Soak Cleaning

- Metals Processed
- Chemistry Requirements
- Displacement or Emulsification
- Operating Limitations
- Rack or Barrel

Are the metals a mix of ferrous and non ferrous types (such as steel copper alloys, and zinc) or just one metal. This influences the soak cleaner selection, as to whether caustic can be tolerated. During the past several years, displacement of oils has become more preferred. Automatic skimming devices such as belts, coalescers, ultrafiltration, tank weirs & overflow dams, are practical aids for displacement cleaning. Whether cleaning is by displacement or emulsification, the oils to be removed should first be tested either in lab simulated cleaning or in line trials to confirm the desired cleaning action is achieved. The next step would be to age the cleaner, thereby confirming on going quality of cleaning effectiveness and maintaining displacement or emulsification. Many process lines have limitations as to time and temperature. This must be included in the evaluation process. Rack or barrel application affects selection by: limitation in rinsing, prevent redeposition of oils on polypropylene barrels, and detergent / solvent capacity to meet on going cleaning demands.

Electrocleaning

- Metals Processed
- Effect of Additional Cleaning & Scrubbing
- Current Densities / Periodic Reverse

- Descaling & Derusting
- Hexavalent Chrome Reduction
- Double Cleaning Cycles

Based on the metals electrocleaned, the alkalinity level is critical. There are three ranges to select, relative to sodium hydroxide (caustic) content: low, mid, or high (<10%, 15-35%, 40-75%). The non ferrous metals (copper alloys, brass, and zinc) are best electrocleaned in the low to mid range sodium hydroxide solutions. These must also contain inhibitors, such as:

- silicate in ratio to caustic for optimum conductivity with sufficient inhibition of the zinc surface.
- Borax buffer and silicate inhibitor for copper alloys and brass, to prevent dezincification of brass and excess oxidation of copper alloys.
- High caustic for steel electrocleaning conductivity requirements. The optimum caustic level also dissolves the iron hydroxide surface film that forms, to prevent splotchy brown stains and burning due to low conductivity.

Current densities are related to the base metal and whether the application is rack or barrel. The action of additives to descale and derust steel can be enhanced by the use of periodic reverse cleaning. Hexavalent chrome contamination is notorious for passivating brass, copper alloys, or steel. Only 25 ppm can be detrimental. The result is plating blisters, peeling, or haze. A secondary problem is reduction of detergency for surface cleaning. Hexavalent chrome contamination occurs typically by: anodic stripping of chrome plated rack tips and parts, drag in of chrome solution inside cracked rack coatings, and stripping chromated racks and danglers. Special additives, added over the side or blended in the electrocleaner formula, efficiently reduce hexavalent chromium to it's trivalent state, precipitating Cr(OH)3. Sometimes double cleaning cycles are best suited to cleaning and activating welded parts, such as wire goods, or heat treated parts.

Acid Pickling & Activation

- Metals Processed
- Acids: Inorganic / Organic
- Effect of Accelerators
- Effect of Inhibitors & Pickling Aids

- Wetting Agents & Deflocculants
- Double Cleaning Cycles
- Stripping Electroplated Deposits

So far the consideration of metals processed is a common factor. Sensitive metals (brass, copper alloys, and zinc) require milder acid treatment. Steels can be scaled and rusted necessitating more aggressive treatment, even cathodic action. Acids can be grouped into inorganic: (hydrochloric or sulfuric) and organic (sulfamic, citric, gluconic, etc...). Accelerators such as chlorides and fluorides provide extra "bite" to improve pickling. Fluorides activate brass by dissolving lead smuts. Inhibitors prevent over pickling steel that would result in raising excessive surface smuts or detrimental hydrogen embrittlement. Pickle aids help two ways: lower solution surface tension to improve wetting and increase contact action. Wetting agents generate a light foam blanket to minimize corrosive sprays and mist, and emulsify residual oils on parts or dragged into the acid bath. Deflocculants prevent the redeposition of soils. Double cleaning cycles may employ an aggressive first acid to meet pickling demands. The second acid should be a milder type sufficient to neutralize the second electrocleaner film while activating the surface, a last step before plating.

Spray Cleaning

- Metals Processed
- Desired or Effective Chemistry
- Low Foaming with Displacement of Soils
- Advantage of Mechanical Action
- Temperature Range

The alkalinity level of the spray cleaner may range from near neutral (approx. 8) to high (at pH=14). This accommodates the type of metals cleaned (aluminum, brass, copper alloys, steel, and zinc). A desired or effective chemistry should be able to lift soils. The surfactants can be low in concentration, since the mechanical action of spraying facilitates dislodging oils and grease. Spray cleaners are best suited to low foaming applications and displacement of soils. A central tank collects the cleaner solution, allowing oils to collect and be skimmed off. This extends service life of the cleaner. It's a real benefit based on the incredible oil loading some incoming parts have. Skimming the cleaner removes the soils, preventing them from being sprayed on dirty parts entering the spray chamber. Water hardness conditioners in the cleaner are invaluable to prevent nozzle pluggage. Spray cleaners are blended to effectively operate at 90-170 degF (32-77 degC), or higher.

Mass Finishing

- Helps with Off line Capabilities
- Cleaning, Descaling, Deburring, Burnishing
- Seals Surface Porosity in Zinc and Aluminum
- Conditions Base Metal Surface

Where applicable, mass finishing invaluably helps condition base metal characteristics. It's a real bonus for surface preparation. This includes cleaning to remove oils and grease, descaling, deburring and rounding out critical areas, and burnishing to a low RMS value or high luster. The process combines mechanical energy and chemical action. Mechanical action is by tumbling in horizontal and oblique barrels or using vibratory bowls. Specially blended chemicals are added in dilute form liquids or low concentration powders. They wet and react with the surface of parts, allowing other parts or special media (e.g. plastic, ceramic, stone) to work on the parts. Mass finishing is especially helpful to seal porosity in aluminum and zinc before transfer to the plating line. If parts are to be mass finished or this is a feasible option, trial evaluations are recommended to determine best suited equipment, media and optimum: media to parts ratio, chemicals, concentrations, flow rates, and cycle times.

Special Considerations

- Steel (low or high carbon)
- Brass (lead content)
- Copper Alloys
- Zinc Alloys
- Aluminum Alloys

Each of these metals and alloy groups exhibit special characteristics or reaction sensitivities. The following sections will highlight important factors related to these metals and alloys.

Beryllium Copper

Alloy Metal	Weight %
Beryllium	2.00
Cobalt	0.25
Nickel	0.35

And other Copper Alloys

Surface Preparation Cycle

- Alkaline Soak Clean to remove organic soils. Mild tarnish is acceptable.

- Electroclean in a specially buffered blend having moderate caustic at 20-40 ASF, anodic.

  Activate in a mildly etching solution composed of peroxy derivatives, persulfates, or sulfuric acid with fluoride.

- Rinse well ...... proceed to plating bath.

Leaded Brass
(0.35 - 4.00% Lead)
Red & Yellow Brasses
Commercial Bronzes

Surface Preparation

- Soak or Ultrasonically Clean to remove buffing & polishing compounds. 20-40 KH/gal. Highly wetted, with solvents, mild alkalinity. Soaps optional.

- Secondary Soak Clean. Surfactants, moderate alkalinity, some inhibition preferred.

- Electroclean. 10 - 30 ASF anodic. Buffered blend similar to use on copper alloys.

- Activate. Sulfuric Acid type containing fluorides, essential to dissolve lead smuts.

Rinse ...... Proceed to plating bath

Bright Dipping Brass

- Mild to moderate alkaline soak clean.
- 5% Sulfuric Acid dip. Neutralize & condition surface.
- Chemically Polish in either peroxide type or Sulfuric Acid/inorganic salt blend. Both types are specially inhibited.
- Bright Dip peroxide polished work to remove skin. Dilute mineral & organic acid mixture.
- Tarnish Inhibit in dip application using either soap or benzotriazole chemistry.
- Optional Tarnish Inhibit using electrolytic chromate.

Inconel

Alloy Constituent	Weight %
Nickel	13.5
Chrome	6.0

Note: one alloy type may contain 2% Silicon.

- Alkaline Soak Clean. Mild to moderate alkalinity with sufficient detergency.
- Acid Dip. 20-30% Hydrochloric Acid, for primary oxide removal.
- Anodic Etch. Woods Nickel Strike at 11- degF, 50 ASF, 20 - 30 sec.
- *Strike Plate. Woods Nickel Strike, 110 degF, 50 ASF, 2 - 3 min.*
- Rinse ...... Proceed to plating bath.

Zinc Alloys

Alloy	% Zn	% Al	% Mg	% Cu	% Pb
Pure	99.9 +	-------------	-------------	-------------	-------------
Zamak 3	balance	4.0	0.04		
Zamak 5	balance	4.0	0.04	1.0	
Zamak 2	balance	4.0	0.03	3.0	
Slush	balance	4.75		0.25	
Slush	balance	5.5			
Drawn	balance				0.08

Zamak 2,5 and the slush castings require mild treatment. The acid should not be too aggressive, otherwise difficult to remove surface smuts will form.

Zinc Alloys
Surface Preparation

- Soak or Ultrasonic clean to remove buffing & polishing cmpds. Wetted with solvents. Soap or mildly alkaline, buffered blend.
- Soak clean to remove residual soils and inhibitor film.
- Electroclean. Moderate alkalinity, inhibited. 20-50 ASF anodic.
- Acid Dip. Fluoboric Acid or Sulfuric/Sulfamic Acid + Fluorides.
- Rinse ...... proceed to plating bath

Aluminum Alloy Designations

Aluminum Alloy Type	Number Group
99% minimum & greater	1XXX
Copper	2XXX
Manganese	3XXX
Silicon	4XXX
Magnesium	5XXX
Magnesium & Silicon	6XXX
Zinc	7XXX
Other Element	8XXX
Unused Series	9XXX

First Digit: Alloy type
Second Digit: Alloy modification

Third & Fourth digit: Aluminum purity of alloy
The significance of each alloy's make up will affect the choice of etchant and desmutter, as indicated in the next sections.

Aluminum Surface Preparation

Basic Cycle

- Soak Clean
- Etch
- Desmut
- Condition
- Plate

Soak cleaning denotes no etching or attack of the base metal. The ideally suited soak cleaner does not contain any caustic or silicate. The solution pH ranges from 8-9.5. Ultrasonic soak cleaners also have a similar chemistry profile. They differ in containing higher detergency levels along with selected solvents. Spray cleaners may also be used, but of lower foaming tendencies.

Aluminum Etching

Alkaline	Acid
Aluminum Alloys Extrusions Stampings	Castings Polished
• High Caustic, aggressive	* Acidic, mild, wetted
• High Caustic, aggressive wetted	* Nitric Acid + Fluoride, mild
• Low Caustic, mild	* Sulfuric Acid mild

Etching is accomplished using acidic or highly alkaline solutions. Etching also cleans the surface by means of undercutting soils and lifting them off. When etched, some alloys (in the 5000, 6000 series and castings) will tend to generate heavy smuts. This can lead to incomplete desmutting, detrimentally affecting the zincate treatment. Acidic etchants, being less aggressive, raise less smut.

Acidic etchants are preferred for conditioning the base metal surface prior to electroless nickel plating.

Aluminum Desmutting

Chemistry Depends on Alloying Elements

- For High Silicon - Sulfuric Acid + Fluorides
- For High Copper - Nitric Acid + Fluorides
- For Low Alloys - Sulfuric Acid + Oxidizers

Desmutting Aluminum

Available Chemistries

- Nitric Acid. Typically 50 - 100%
- Nitric Acid + Fluorides
- Nitric Acid + Sulfuric Acid
- Nitric Acid + Sulfuric Acid + Fluorides (Universal Tri Acid). Removes smut with no further attack.
- Dichromates + Fluorides

Examples of surface preparation cycles for special aluminum parts:

Aluminum Wheels
356 Alloys

- Spray or Ultrasonically Clean.
- Non Etch Soak Clean.
- Acid Etch.
- Desmut

- 1st Zincate
- Strip Zincate
- 2nd Zincate
- Strike

Aluminum Bus Bars / Connectors

- Non Etch Soak Clean.
- Alkaline Etch
- Desmut
- Zincate
- Strike: Non Cyanide Copper or Bronze
- Acid Tin Plate
- Bright Dip

Quality and Integrity of the Finish

During and following completion of the process cycle, specific tests *are conducted to determine the degree of quality. Examples of these are listed* below. The first, second, and third tests focus on determining cleanliness. The fourth test is an aggressive evaluation of adhesion, where actual parts, test pieces, or hull cell panels are sacrificed. An overall visual inspection should confirm the presence or absence of deposit streaks, haze, and blisters. Each proprietary bath should be selected based on trial or lab evaluations. The optimum time, temperature, and concentration should be determined. All process baths should be regularly analyzed, making the appropriate maintenance additions. Record keeping is essential to track operating history, occurrence of problems, and corrective action. Service life should be determined and adhered to. Rinsing cannot be overemphasized.

Test It Yourself

- Water Break Free Observation
- Immersion Copper deposit
- Ultraviolet Light Test
- Post Plate Bake, Grind, or Bend
- Inspect Finished Quality

All the process cycles described have some common relationships. The bath chemistries must conform to processing the specific metal in the particular conditioning step. Where different metals are processed in the same line, the soak cleaner, electrocleaner, and acid must be flexible to handle them all (e.g. ferrous and non ferrous). If rinsing or process baths are limited, an appropriate combination soak / electrocleaner can be used. In some plating lines, the particular base metal conditioned will be the only one, simplifying selection of baths.

To Process Parts Right ... Start Off Right

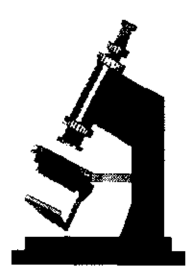
Cleaning & Activation

That First Big Step Towards a Great Finish

Every Finisher's Goal

Do It Right at

AESF SUR FIN '99



Observation ... Innovation ...Results