

# **FINISHING OF ALUMINUM**

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**10/1/24**

Please note that the intent of this article is to provide guidelines. Specific information and/or parameters may vary with the aluminum alloy, the condition of the work surface following machining, extruding or casting, geometry of the parts and/or the specific design of the process line. In addition, individuals often have their own ideas and methods... and with anodizing, there is “more than one way to skin the cat”. The information contained herewith should be verified for each application.

Aluminum has become a very valuable metal for manufacturing companies in the aerospace and other industries due to its low cost, excellent weight-to-strength ratio and ease of machining and fabrication.

Aluminum is the third most abundant element in the Earth’s crust, after oxygen and silicon, its commercial use is relatively “new”, becoming available in commercial quantities and at a reasonable cost just over a century ago. This is because Aluminum is produced only by a complex process that uses huge amounts of electricity (approximately 17,000 kilowatt-hours per ton of Aluminum). As an amphoteric metal which can react with an acid as well as a base, aluminum is very reactive. As a result, it is found in over 270 natural occurring minerals. The chief ore of aluminum is bauxite.

As the element, aluminum has a relatively low strength and hardness but does have extreme flexibility and ductility. However, it has virtually no structural strength and therefore few industrial applications.

As a result, aluminum is alloyed with various other metals to modify its properties. The most common alloying elements are copper, magnesium, manganese, silicon, tin and zinc. There are two principal classifications, namely casting alloys and wrought alloys. Because wrought alloys offer greater strength, they are significantly more common in industry. There are over 100 recognized casting alloys, and more than 400 wrought Aluminum alloy designations. Among the most common wrought alloys used in industry are 2024, 5052, 6061, 6063, 7010 and 7075. The most common casting alloys are 356 and 380.

The alloy will affect how it finishes, most commonly:

- Voltage in anodizing
- Color of the clear anodic coating
- Color of the dyed anodic coating
- Time to build a specific anodic thickness
- Time to obtain a specific coating weight in chem film
- Coating weight in chem film

As far as finishing, the most common coatings or processes applied to aluminum are:

1. Paint
2. Chem film
3. Anodizing
4. Plating

## 5. Spot welding

Typically, prior to painting, the aluminum will be coated to improve adhesion &/or undercoat corrosion should the paint coating be damaged. Two common paint pre-treatments for aluminum are chem film and Type II anodizing. Occasionally, an iron or zinc phosphate coating is applied prior to painting as well as relatively new fluoro-based chemical processes that utilize zirconium, vanadium, titanium or silicon-based compounds with or without organic binding compounds.

As noted, chem film is a very common paint pretreatment but can also be used as a stand-alone coating to improve corrosion resistance. Chem film is also used for corrosion resistance when it is important to maintain surface conductivity with minimal electrical resistance.

Anodizing is used for a variety of reasons:

- Improved corrosion resistance
- Improved paint adhesion
- Decorative finishes by applying a wide variety of colors
- Part identification by applying specific colors to indicate size, alloy or design
- Increasing the surface hardness for better wear properties

Due to its reactivity, aluminum must be coated with a less reactive metal prior to electroplating. The most common metal used today is zinc. However, in years past and for specialized application, tin has also been used. Aluminum is generally coated with these metals using an immersion or galvanic process rather than an electrolytic process. However, it can also be coated using an autocatalytic or electroless process with the most common metal used in this approach being nickel.

## **VARIATIONS IN THE ALUMINUM ALLOY**

When processing aluminum, for any of the processes discussed below, it is important to know the alloy and the temper of the substrate as these may require “tweaking” the process parameters to obtain the desired finish. Furthermore, variations in the lot to lot processing of alloys can also impact your results. It is highly preferred to use one source to provide the aluminum substrate and even then, you may have minor variations in how the aluminum performs in your process.

## **NATURAL OXIDE FORMATION**

An oxide film will develop immediately on aluminum when exposed to atmospheric oxygen. Aluminum oxide has the chemical formulation  $Al_2O_3$ . It will build to about 2 to 3 nanometers within a couple of days and reach a maximum thickness of about 5.5 to 6 nanometers (one micron or  $\mu m$  is 1000 nanometers). Because it is adherent, it will provide some corrosion protection as long as this oxide layer is stable and undamaged. Pure aluminum shows the highest corrosion resistance by forming a very uniform natural oxide layer. However, as alloying elements are added, this resistance decreases because of inconsistent thickness and porosity. Therefore, to protect the metal for industrial applications, the thickness and uniformity of the oxide coating must be significantly increased. The most common method to increase the thickness is anodizing.

## **THE ELECTROLYTIC CELL (I.E. THE ANODIZING TANK)**

Anodizing occurs in an electrolytic cell which has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually an aqueous acid in which positive and negative ions are dissolved. When driven by an external voltage applied to the electrodes, the ions in the electrolyte are attracted to an electrode with the opposite charge, where charge-transferring or redox reactions can take place. The cathode is defined as the electrode to which cations (positively charged ions) flow within the cell, to be reduced by reacting with electrons (negatively charged particles) from that electrode. Likewise, the anode is defined as the electrode to which anions (negatively charged ions) flow within the cell, to be oxidized by depositing electrons on the electrode. Thus, the cathode is positive and the anode is negative. In an aqueous solution, oxygen is generated at the cathode and hydrogen is often generated at the anode. In anodizing, the aluminum oxide is formed at the anode, along with a small volume of oxygen, and hydrogen is formed at the anode.

The electrolytic cell will behave according to Ohm's Law.... that is voltage = resistance x current. For a given voltage, as the resistance changes, the current changes. The important thing to understand here are the factors that contribute to the resistance within the cell.... busing, tooling, electrolyte parameters (concentration & temperature) and oxide thickness.... are dynamic and continually changing. Therefore, required voltages and amperage will change to achieve a given result. When anodizing, this is important to understand because the voltage is the primary factor to determine the coating.

Current flow within the electrolytic cell will follow Ohm's Law.... that is current will follow the path of least resistance. This means the current per surface area or current density will vary across the surface of a part within the electrolytic cell. Therefore, the reaction will occur in areas of high current density first and as the anodic coating builds, the resistance of the coating increases forcing the current to flow to areas of the part that are lower current density. As a result, because the oxide coating is a dielectric, the coating thickness in an anodizing process under constant voltage conditions will build to a very uniform coating thickness.

## **WHAT IS ANODIZING**

Simply stated, anodizing is the process of forming an aluminum oxide on the surface of the metal. Being very reactive, aluminum will naturally form an aluminum oxide layer very quickly. However, this natural coating is typically very thin and inconsistent. Therefore, we place the metal into various electrolytes, primarily conductive acids, and apply a cathodic current to force the oxide layer to grow. The thickness and density of this oxide layer give the anodized coatings its properties. By changing the properties of the electrolyte and the parameters of the anodizing process, we can adjust the thickness and density, or more commonly termed... the porosity of the deposit. During anodizing, two competing reactions are actually occurring.... we are forming the oxide coating and the electrolyte is dissolving the oxide coating. By controlling the rates of these two reactions, we develop the coating properties that we seek. We can increase the formation by manipulating the current. We can increase the dissolution by increasing the temperature of the anodizing bath, changing the concentration of the anodizing bath and changing the nature of the acid used for the anodizing bath. Conversely, we can decrease the dissolution by decreasing the temperature, decreasing the acid concentration and changing the acid. The more porous the deposit, the softer the anodic coating and the lower it's corrosion protection.... but the more readily the coating will absorb a dye. Conversely, the less porous the deposit, the harder the anodic coating and the better the corrosion resistance.... but the more difficult it is to dye.

In summary, as you increase....

**Acid Conc.**

**Temperature**

**Current Density**

Dissolution	Increases	Increases	Decreases
Pore Size	Increases	Increases	Decreases
Hardness	Decreases	Decreases	Increases
Thickness	Builds Slower	Builds Slower	Builds Faster
Clarity of Coating	Clearer	Clearer	Less Clear

Conversely, as you decrease....

	<u>Acid Conc.</u>	<u>Temperature</u>	<u>Current Density</u>
Dissolution	Decreases	Decreases	Increases
Pore Size	Decreases	Decreases	Increases
Hardness	Increases	Increases	Decreases
Thickness	Builds Faster	Builds Faster	Builds Slower
Clarity of Coating	Less Clear	Less Clear	Clearer

There are several types of anodizing commonly used in the industry:

- Type I Chromic Acid      Used as a corrosion coating and to deposit a hard deposit, especially on parts with adjacent surfaces that could trap solution by capillary action (any residual chromic acid will passivate the aluminum where as other trapped acids can cause corrosion of the aluminum).
- Type II Sulfuric Acid      Used as a corrosion coating, paint adhesion and decorative coating.
- Type III Sulfuric Acid      Used as a corrosion coating and to deposit a hard deposit.
- BSA (Boric Sulfuric)      Developed by Boeing to replace Type I to eliminate the need for hexavalent chromium.
- TSA (Tartaric Sulfuric)      Developed by Airbus to replace Type I, again to eliminate hex chrome.
- PAA Phosphoric Acid      Used primarily to enhance the adhesion of adhesives when bonding composites to aluminum.

The primary difference in the anodic coating produced by each type of anodizing process is the size of the pores within the coating. As pore size increases, the thickness of the coating becomes more limited, the hardness of the coating decreases, the ability to absorb dyes increases and the corrosion resistance decreases. On the opposite side of the coin, each of the above parameters change in the opposite direction... the thickness of the coating can increase, the hardness increases, the coating does not absorb dyes as well and the corrosion resistance increases.

Anodizing and chem film react with the aluminum in the substrate but not the metals that are alloyed with the aluminum. As a result, the different alloys of aluminum will impact the results that are obtained in these processes. Therefore, the cosmetics of the finish and the corrosion of the finish will be affected by the alloy,

## **SURFACE PREPARATION**

The work surface shall be clean of lubricants, coolants, fingerprints, alloy marking ink and significant oxides. This cleanliness is best evaluated using a water break test.... a surface that maintains a continuous water film for a period of at least 30 seconds after having been spray or immersion rinsed in clean water at a temperature below 100°F is considered clean and ready for surface finishing.

The most common preparation for wrought aluminum alloys would be:

- Soak clean using an inhibited alkaline cleaner
- Rinse

- Alkaline etch
- Rinse
- Deoxidize

An alternative preparation often used if soils are minimum would be:

- Acid clean
- Rinse
- Acid etch
- Rinse

The most common preparation cycle for cast alloys would be:

- Soak clean using an inhibited alkaline cleaner
- Rinse
- Tri-acid etch (chromic acid, nitric acid & hydrofluoric acid)
- Rinse
- Desmut (nitric acid)

In most all preparation cycles, the initial step is the removal of surface soils on the part.... lubricants, coolants, ink from metal markings, fingerprints and shop dust and dirt. A clean surface is necessary to assure that the following etch, desmut and deoxidizing processes can occur with uniform results across the surface.

Inhibited cleaners are typically more effective at cleaning heavy soils because they can be formulated with more alkalinity. However, the most effective inhibitors are silicates which, as you will see later, are disruptive to the etch, anodizing, dying and sealing steps. Silicates are difficult to rinse off and can contaminate these following processes. Most cleaners therefore use silicate free inhibitors.

Another choice in soak cleaners is whether to use an emulsifying cleaner or non-emulsifying cleaner. The former will effectively break up the oil into fine particles which they can then effectively hold in solution. The latter will remove the oils from the work but allow them to float to the surface of the cleaner. Even emulsifying cleaners will reach saturation and eventually allow oils to float and some oils will not emulsify. Therefore, all cleaner tanks should have an overflow weir with continuous recirculation to skim the surface and accumulate soils in the weir.

Acid cleaners can result in a shorter process line and require less rinsing before the acidic deoxidizer, anodizing and chem film steps. Phosphoric acid cleaners should be avoided since the phosphates are not only disruptive to the anodizing processes, they can be an ecological problem as well. Sulfuric acid based cleaners are more acceptable but have limited cleaning capacity. Therefore, acid cleaners are generally only successful if the work has been pre-cleaned prior after machining and prior to processing so that the soils are very light.

Once the surface is clean, removal of the natural oxide coating is key to the successful adhesion and appearance of the coating applied to the aluminum. The most common method to remove the light surface defects and heavy oxide coatings is alkaline etching followed by an acid desmut or deoxidizing step. More information is provided below on etching aluminum. The key to remember, the surface has to be clean of soils and have a uniform natural oxide to promote uniform etch.

For most preparation cycles, the removal of the oxide coating occurs with relatively short immersions times and ambient to moderate temperatures. The degree of etch is highly dependent on the Quality of the substrate finish. To provide a premium visual appearance, etching is performed to minimize or

eliminate surface defects such as shadow lines, flow lines, die lines, and light surface scratches. The more surface defects that have to be removed, a more aggressive etch that is required. This more aggressive etch is generally achieved by balancing an increase in temperature with an increase in immersion times. As a result, etch times will generally vary from 3 to 15 minutes and temperatures from 100°F to 140°F.

Desmutting removes excess alloyed metals from the surface of aluminum after etching. Alloyed metals will vary depending on the aluminum alloy but the most common are Silicon, Magnesium, Copper, Zinc, Nickel, Manganese and Tin. Desmutting can be often be done using any mineral inorganic acid, such as hydrochloric, sulfuric and/or nitric acids.

Deoxidizing is removing the aluminum oxide off the aluminum substrate via oxidation-reduction (redox) reactions. Aluminum inherently protects itself from by readily oxidizing and creating a very thin layer of aluminum oxide when it comes in contact with the surrounding oxygen. This layer of oxide is not of a sufficient thickness or uniformity to serve most applications and in fact, interferes with most all subsequent finishes that we would want to process aluminum with. Thus, we need to remove it with a solution referred to as a deoxidizer.

In most aluminum finishing lines, both desmutting and deoxidizing will occur in the same proprietary chemistry.

As noted above, specific alloys and tempers may require variations in the above parameters. These variations are probably most evident in the cleaning and preparation of the substrate for the subsequent finishing.

## **RINSING**

Rinsing is a critical step for anodizing and chem film process lines. So, while you need excellent rinsing, as with all finishing processes, you need excellent efficiency because every gallon of rinse water is a potential gallon of waste to be treated. The cost of waste treatment can exceed the cost of the water itself. Furthermore, many locales have a “tax” on the volume of water discharged to the sewer. So efficient rinsing is critical for economic production.... but poor rinsing due to low water flow will often result in more costs than the cost of the water and treatment.

Common impurities in water.... calcium, magnesium, sulfates and chlorides.... to one degree or another are all disruptive to the processes. Furthermore, rinse water is dragged into the following process tank so both the Quality of the rinse water and the Quality of the rinse process is dependent on the nature of the following process. As a general rule, the preparation processes.... clean, etch, desmut and deoxidize.... require less rinsing Quality than the deposition processes that follow.... chem film, anodizing, dyeing and sealing. For the deposition processes, depending on incoming water quality, it may be necessary to pre-treat the water, typically using reverse osmosis or ion exchange.

Therefore, with any amount of production capacity, counterflow rinsing is highly recommended to assure efficient use of water. However, if the rinse tank is small enough, it usually does not take a lot of water to have a short tank volume turnover.... that is, the length of time it takes to add the tank volume as rinse water flow. As a result, with small tanks, counterflow rinsing may not be necessary.

Another exception is when ion exchange is being used to purify and recycle the water. With the use of IX, static drag-out rinses must be utilized following most all of the chemical process tanks. The exceptions are the nickel acetate seals and dye tanks which are not very concentrated and the nitric acid dye activator that does not get rinsed. Since the waste from the drag-out tanks is treated in the batch treatment proposed system, they are used to control the ionic content that reaches the flowing rinses, which in turn determines the frequency that the ion exchange proposed system is regenerated. The more frequently the drag-out tanks are diluted or dumped, the lower the equilibrium concentration within the tank. The lower the equilibrium concentration, the less ions that are dragged into the rinses. Conversely, the less frequently the drag-outs are diluted or dumped, the higher the equilibrium concentration and the more ions that are dragged into the rinses. The more ions that are dragged into the rinses, the more frequent the IX proposed systems have to be regenerated. Therefore, using this logic, controlling the frequency that the drag-out tanks are diluted or dumped can control the frequency of regeneration.

Rinses following alkaline chemistries perform best when heated to between 80°F and 90°F. Tempered water rinses alkaline films more efficiently than cold water.

The most critical impact on the volume of water that is required for Quality rinsing is the drag-out from the preceding chemistry tank. This drag-out is dependent upon a number of parameters:

- ✓ The geometry of the part
  - + Deep recesses &/or internal surfaces requires more rinse water
  - + Areas that cup solution requires more rinse water
  - + Blind holes requires more rinse water
  - + Crevices that capture solution by capillary action requires more rinse water
  - + Horizontal surfaces requires more rinse water
  - Vertical surfaces requires less rinse water
  - Edges to drip off requires less rinse water
  - Corners to drip off requires less rinse water
- ✓ The orientation of the fixturing of the part
  - The orientation should enhance the above “–“ features and minimize the above “+” features
- ✓ The surface area of the part
  - The greater the surface area, the greater the drag-out and the more water that will be required
  - Conversely, the smaller the surface, the less the drag-out and less water is required.
- ✓ The concentration of the chemistry
  - The greater the concentration, the greater the drag-out and the more water that will be required
  - Conversely, the lower the concentration, the less the drag-out and less water is required.
- ✓ The viscosity of the chemistry
  - The greater the viscosity, the greater the drag-out and the more water that will be required
  - Conversely, the lower the viscosity, the less the drag-out and less water is required.
- ✓ The speed at which it is withdrawn from the solution
  - The faster the work is withdrawn, the greater the drag-out and the more water that is required.
  - Conversely, the slower the work is withdrawn, the lower the drag-out and less water is required.
- ✓ The length of available drip time
  - The shorter the drip time over the chemistry tank, the more the drag-out and the more water that is required.

- The longer the drip time over the chemistry tank, the less the drag-out and less water is required. However, care must be taken to eliminate staining due to drying of the work.
- ✓ Misting over the chemistry tank during lift and drip time can reduce drag-out by lowering the concentration and viscosity to improve the efficiency of the drip off time.
- ✓ Agitation in a rinse tank decrease the volume of water required.
- ✓ The design of the rinse tank
  - Small tank volume results in less water
  - + Large tank volumes large tank volume required more water
- ✓ The type of rinsing scheme
  - Spray rinsing generally has limited efficiency and should only be used for flat, vertical parts. If spray rinsing is used, it should be pulsed on and off in intervals of about 5 seconds on and 10 seconds off. Spray rinses do offer the advantage that multiple chemistries can be rinses without worry of cross contamination.
  - Exit sprays are generally not that efficient because the work passes through the spry very quickly.
  - Double counterflow rinsing is generally very efficient in most applications.
  - Triple counterflow rinsing is generally efficient only in very high production situations

The water Quality for rinsing is often specified in work specifications and will vary by specifications. Typically, rinses between processes should be maintained between 500 and 1000 PPM of dissolved solids. Final rinse should be maintained between 300 and 500 PPM.

While the immersion time in rinses is often not critical, there are factors that can affect how long the work should spend in the rinse tank. With good agitation, the contaminants on the work surface is often diluted to equilibrium with the rinse water quite fast and in many cases, rinse times of 30 seconds are sufficient. However, if the work geometry is complex with deep recesses, internal surfaces and/or blind holes, longer immersion times may be required. In addition, the temperature of the rinse water will impact time with colder waters requiring more time. Since the aluminum surface is reactive, you do not want to spend too long in the rinse tank. This is especially true after the etch, desmut and deoxidize steps.

## **BRIGHT FINISHING**

For decorative finishes, prior to anodizing, parts are often treated chemically or mechanically to achieve either a bright, smooth reflective surface.

Typically, for a bright finish, the aluminum is immersed in an aggressive mix of phosphoric and nitric acids. This levels out the microscopic, rough peaks and valleys on the aluminum surface and makes it very bright and reflective.

While 6061 and 6063 are among the most common alloys anodized, unfortunately these do not develop highly smooth and specular finish when bright dipped. These alloys can be used for a bright cosmetic finish but will not serve for a reflective application such as lighting. One of the best alloys for bright dipping is 6463 aluminum. It is a variant of 6063 and has similar properties but was specifically developed for bright dip applications.

While you can find a variety of formulations, the most common is generally referred to as an R5 bright dip and consists of 75% to 85% b.v. concentrated phosphoric acid and 2% to 5% b.v. concentrated nitric acid and the balance DI water. You can also find similar formulations that utilize sulfuric acid and possibly acetic acid. Nearly all of the formulations operate between 195°F and 210°F. Please remember that specific alloys and tempers may require variations in the above parameters.



Prior to bright dipping, it is important that the aluminum surface be clean and free of oils, coolants, lubricants and/or marking inks. If the soils are not extensive, it may be advantageous to utilize an acid cleaner; however, acid cleaners have a limited ability to clean heavy soils. More often, the standard preparation is a non-etching or low etching alkaline cleaner followed by a light etch in an alkaline etch followed by a deoxidizer to remove copper and other alloying metals from the surface.

Due to the viscosity of the solution, extensive rinsing is required following the process step. As a minimum, it should include two or three steps of counterflow rinsing with enhanced agitation and slightly linger immersion times.

It should be noted that these bright dip processes require special attention to the equipment. Many of these processes operate in an insulated, 316L tank; however, this material is generally rated as a “B” or “C” on most corrosion charts and can/will eventually fail. It would be recommended, despite the cost, to make the tank out of PVDF or use a PVDF liner.

Furthermore, of greater concern, is the design of the ventilation system. Due to the nitric content, these processes will generate NOx fumes that will emanate from work in the raised position. In addition, NOx is also generated at the rinse that follows the process. In addition to being an air pollutant when released into the atmosphere, NOx fumes are also toxic to the operators. The discharge requirements vary from region to region, many air quality districts will have a limitation. Please be aware that NOx vapors are not visible as orange-to-brown vapors below about 75 ppm.

Since it comes off the work in the raised position, standard exhaust designs may not capture these toxic fumes. Therefore, the tank is often located within a confined enclosure with walls generally on three sides and a ceiling. Finally, depending on the size of the operation and upon your local air quality management district, special steps may have to be taken to remove the NOx from the discharged exhaust. A standard wet scrubber may remove up to 20% of the NOx and with an extended bed and high recirculation rate, a packed bed scrubber may get 50% to 60% of the fumes. To fully remove the fumes, a two step and even three step scrubber is required and will operate with a reducing agent in the reservoir.

Please note that, due to the high temperature and strong acids, special safety precautions should be taken in the area of this operation. We would recommend a dedicated safety shower and eye wash, which with today’s requirements, must use tempered or heated potable water. Operating personnel should wear appropriate PPE.... apron, gloves and face shield as a minimum.

A bright finish can also be achieved using an electropolish process which offer a significant reduction in safety concerns as it operates at room temperature and eliminates problems with the NOx fumes. In addition, proponents of electropolishing will claim lower costs as well as easier process control. As with the chemical bright dip process, electropolishing will also “level” out the surface to remove minor imperfections.

It is performed with reverse, direct current and is essentially, a “backwards” plating operation. The tank is fabricated from insulated, 316L stainless steel and is often used as the cathode in the DC circuit. The parameters, while similar, do vary from the more common electropolishing of stainless steel. A summary would be:

<u>Parameter</u>	<u>Stainless Steel</u>	<u>Aluminum</u>
Temperature (°F)	120 to 125	150 to 185
Voltage (Volts)	6 to 9	10 to 24
Amperage (ASF)	5 to 15	20 to 50

Time (Minutes)	4 to 10	2 to 15
Agitation (Preferably by Pump)	None to Low	Vigorous
Generic Chemistry	Sulfuric w/ Additives	Sulfuric, Phosphoric & Nitric

A common recipe would be 70% b.v. concentrated sulfuric acid, 15% b.v. concentrated phosphoric acid and 1% b.v. concentrated nitric acid with the balance DI water.

There are reports of the use of a process using sodium carbonate/trisodium phosphate as the electrolyte but this is less common.

## **MATT FINISHING**

While matt finishes are generally achieved by using alkaline etches to dull the finish, it is also possible to use a fluoride based, acidic solutions to provide a finer etched finish with smaller grain texture. With conventional caustic etching, upwards of 10 gm/sq.ft. of aluminum is etched away from the surface. With acid etches, only about 1gm/sq.ft. is removed from the surface of the aluminum, cutting etching times significantly. Thus, acid etches are generally faster than alkaline etches. In addition, these acidic processes lead to a more consistent, matte finish.

The chemistry of the sodium hydroxide-based etching process for aluminum is complex. The basic reactions are that of sodium hydroxide (caustic soda) plus water and aluminum react to produce sodium aluminate and hydrogen. The pH bath of the bath is highly alkaline so the sodium aluminate will “hydrolyze,” or react with the water to form free sodium hydroxide and aluminum hydroxide. The aluminum hydroxide is insoluble and will precipitate as a very hard scale on the bottom of the tank and often walls. This scale is not easily removed so most companies use a proprietary etch that contains a sufficient concentration of chelating additive to hold the dissolved aluminum in suspension. Without the proper additives, the caustic soda etching bath will only hold about 20–25 g/l of dissolved aluminum. With the addition of the chelating agents, the bath can often keep up to 200 g/l or more of dissolved aluminum. However, as the dissolved aluminum builds up in the bath, the bath becomes quite viscous. This increases the amount of solution drag out which, in turn, helps keep the amount of dissolved aluminum in a range of equilibrium, usually between 120 g/L and 150 g/L. Often, it is necessary to add surfactants to decrease the viscosity and drag-out so that excessive amounts of bath solution are not lost. There are additional chemicals added to help prevent preferential etching.

When not in use, the bath must be kept near operating temperature and must have fairly vigorous agitation to help maintain the chemical balance. If properly maintained, etching baths can last for years without ever having to be completely dumped and made new. Maintaining proper concentration of caustic soda and additives, holding the correct temperature range and always having agitation are necessary for proper bath maintenance.

Essentially, the more complexed aluminum that there is in the bath, the less aggressive the etch will be and the more “satin” the finish becomes. As the dissolved aluminum increases, it is recommended that the concentration of NaOH be incrementally raised as well. A good starting point for a new bath is 50 g/L (7 oz/gal) with the caustic often being raised to about 75-85 g/L (10-12 oz/gal) to maintain the degree of etch. This also helps the bath retain more aluminum. However, at some point, the dissolved aluminum may start causing a surface condition called “spangling” or “galvanizing” which will in turn cause a cosmetic rejection following anodizing, dying and/or chromating. This defect can also be caused by high zinc concentrations in the etch bath. The zinc concentration should ideally be kept below 3 to 4 g/l.

Most etching baths that have high production throughput should be decanted two to four times per year to keep the NaOH and dissolved aluminum concentrations within proper range and help remove other alloying elements and contaminants.

In addition to creating matt finishes, caustic etches are often used to control dimension and remove aluminum for weight savings. This process is commonly referred to as chem mill etching. In past years, it was far more commonly used in the aerospace industry; however, with the advent of highly capable machining tools, this process has often been replaced by multiple dimension, computer controlled milling machines.

Quite frequently, when a matt finish is desired, an acid fluoride etch will be utilized. This acid etch provides a finer crystalline structure than the common alkaline etchants. In addition, the alkaline etchants may bring out the grain structure of the aluminum more readily than the acid etchants.

A typical formulation would be:

<u>Parameter</u>	<u>Value</u>
Fluoride concentration (g/l)	12.3
Fluoride concentration (oz/gal)	1.5
Temperature (°F)	Ambient
Immersion Time (Minutes)	3 to 6
Agitation	Mild (Preferably by Pump)

The fluoride can be derived from hydrofluoric acid but the use of ammonium bifluoride is significantly safer to handle.

Please remember that specific alloys and tempers may require variations in the above parameters.

Please note that, due to the high fluoride concentrations, special safety precautions should be taken in the area of this operation. We would recommend a dedicated safety shower and eye wash, which with today's requirements, must use tempered or heated potable water. Operating personnel should wear appropriate PPE... apron, gloves and face shield as a minimum.

Mechanical finishing with abrasive blasting using either glass bead or aluminum oxide can also produce an attractive matt finish, although not as smooth or fine as the chemical etches. If a mechanical blasting is used, it is highly recommended that the media be used only for aluminum; otherwise, you can transfer contaminants into the surface of the soft aluminum. In addition, the blasting will cause the surface to be work hardened which can affect the uniformity of any subsequent chemical treatment.

## **PROCESSING ALUMINUM CASTINGS**

Aluminum castings must be prepared for anodizing or chromating with a significantly different approach than wrought alloys. Castings must not be etched in an alkaline etch. A casting has significant areas of silicon on the surface. This is necessary to allow the aluminum to separate from the molding material in which it was cast. In the case of a sand casting, it comes from the silica in the sand mold. Finally, it is added to the aluminum alloy to increase fluidity of the molten aluminum. In preparing the casting for processing, you not only want to remove soils from the surface, you also want to remove the silicon.

When you use an alkaline etch, the chemistry preferentially attacks the aluminum on the surface so it actually increases the concentration of the silicon on the surface. Instead, you want to use an acid etch with a fluoride to attack the silicon. The most common etch for castings is a mixture of nitric acid and fluoride ion. Since hydrofluoric acid is extremely dangerous, most finishers choose to provide the fluoride using the dry salt of ammonium bifluoride. Often, superior results can be obtained by using a “tri acid” formulation. Tri acid formulas can vary but most frequently refer to nitric acid, chromic acid and fluoride or nitric acid, sulfuric acid and fluoride. While the former is often considered more effective, the use of hexavalent chemistry has limited its use.

Castings will have more surface porosity than wrought alloys. As a result more aggressive rinsing with longer immersion times and tempered water temperatures (80°F to 90°F) will be required. In addition, they will often require greater currents in the anodizing process.

## **TYPE I CHROMIC ACID ANODIZING**

Due to the toxicity of the hexavalent chromium, most applications that remain are for government and military applications. As a result, Type I anodizing is becoming less and less common.

In addition, chromic acid anodizing is generally accepted on a limited number of aluminum alloys. From Mil 8625, it states that, unless otherwise specified, Type I coatings should not be applied to alloys with a nominal content of more than 5.0% of copper, 7.0% silicon or total alloying metals of 7.5%.

Type I or Chromic acid anodizing produces the thinnest anodic coat of the principal or three most common types of anodizing... Type I, Type II or Type III finishes. Thicknesses are typically on the order of .00002”-.0001” (20 to 100 microinches) per surface. While thin, when properly sealed, chromic anodize affords the aluminum equal corrosion protection to the thicker sulfuric and hardcoat type anodize.

Type I coatings are usually gray in color and being thinner, absorbs less color when dyed. Therefore, Type I anodizing is limited generally used as an industrial finish. However, these finishes can be dyed black and are often used as a non-reflective, protective coating on housings for optical components. When dyed, Type I finishes are lighter in appearance (grayer) than black Type II sulfuric anodized finishes. To enhance the coating’s ability to accept black dye, the temperature of the chromic acid must be raised to increase the porosity.

One characteristic of Type I coatings, which is both an advantage and disadvantage, is the residual hexavalent chromium that is in the coating. It is an advantage in that it inhibits corrosion on parts that are highly stressed and on parts with a geometry that may trap residual process chemistries. However, it is a disadvantage in that hexavalent chromium is toxic to humans as well as the environment.

The fatigue resistance of chromic acid anodizing is quite high when compared with that of sulfuric acid coatings because chromic acid films are more flexible and they are normally very thin. The heavier the anodic coating, the less fatigue resistance the part will have.

Type I coatings typically provide the best corrosion protection as evaluated by salt spray.

### **Characteristics of Type I Chromic Acid Anodize:**

- Good for tight tolerance parts because dimensional changes are minimal
- Good for bonding
- Non-conductive
- Good for welded parts and assemblies

The most commonly used parameters for Type I Chromic Acid Anodizing are:

• Chromic acid	High Conc. 12.3 oz/gal Low Conc. 3.7 oz/gal.
• Maximum Aluminum Content	
• Maximum Copper, Nickel & Manganese Content	
• Maximum Chloride & Fluoride Content	less than 0.02%
• Maximum Sulfate Content	less than 0.05%
• Maximum trivalent chromium concentration	<2 g/l
• Maximum Iron Content	
• Temperature:	High Conc. 125°F to 130°F Low Conc. 92°F to 105°F
• Agitation:	Solution agitation w/ eductors
• Filtration:	Optional
• Ventilation	Required
• Voltage	42-48 Volts
• Amperage	1 – 10 ASF, Typically 3-5 ASF
• Thickness	1.27 μ - 12.7μ to (0.00005”- 0.0002”)
• Anodizing Rate	
• Ramp (V/Min.)	10 minutes at 4 V/Min.
• Voltage control	
• Cathodes	316L SS or carbon steel
• Typical Anodizing Time	20 to 40 minutes
• Optimum salt spray performance	336 hours of salt spray resistance per ASTM B 117

### Notes

1. The higher concentrations are for thicker oxides while the lower concentrations produce a harder and more compact oxide. There is little difference in the operation of the bath as the concentration is increased above 10%.
2. Castings will require significantly higher current densities and are more successfully anodized using the lower concentration bath at 30 to 35 volts.
3. Excellent for anodizing aluminum parts that are to be riveted together or that form lap joints. Because the chromic acid does not attack the aluminum, thorough rinsing and neutralization of the acid in lap or riveted joints is not as critical.
4. Due to the toxicity of hexavalent chromium, this anodizing process is the most difficult to permit with the various regulatory agencies.
5. Again, due to the hex chromium, this process also requires greater capital costs in equipment. It is likely that you will need a HEPA filtration on the exhaust. It may also be necessary to eliminate air agitation and then use large eductor pumps to generate solution agitation. The rectifier and cooling requirement are greater than most of the other anodizing processes.
6. Trivalent chromium is re-oxidized at the anode or work. Excessive cathode area can lead to increased trivalent concentrations.
7. Typically, only dark red or black dyes provide an acceptable finish due to the color of the initial anodic coating. The Type I coating does not readily absorb dyes. Typically, dyeing occurs at higher concentrations of dye, higher temperatures and longer immersion times. It may be helpful to use a dilute nitric dip to open the porosity of the coating; however, this can have a small detrimental effect on the hardness and corrosion resistance of the coating.

## **TYPE II SULFURIC ACID ANODIZING**

Type II sulfuric acid anodizing is the most common method of anodizing. Coatings from this process typically range from .0001"-.001" (2.54μ - 25.4μ) thick. The overall thickness of the coating formed is 67 percent penetration in the substrate and 33 percent growth over the original dimension of the part.

The most common application of this coating is as a decorative finish. Because of the porous nature of the coating, prior to sealing, it absorbs dyes very well. This opens the door to a wide variety of colors from yellow, golds, greens, blues, browns to black.

As noted above, prior to anodizing, parts can be treated chemically or mechanically to achieve either a bright, smooth reflective surface or a matte, non-reflective surface.

The sealing after dyeing helps increase corrosion protection and serves to prevent color loss from exposure to UV light particularly in outdoor service. As a generality, dyes that utilize organic pigments offer better UV resistance than dyes that utilize organic pigmentation. For the ultimate UV stability, it is generally accepted that electrolytic dyes using tin-based chemistry provide the best service. These dyes, often referred to as two-step anodizing, are used extensively in the architectural industry.

Type II finishes are particularly suited for applications where hardness and resistance to abrasion is required. However, where parts are subjected to considerable stress, (such as aircraft parts), the possible presence of the corrosive acid residue is undesirable.

Due to its ease of operation and its lack of hexavalent chromium, Type II finishes are often used for pre-paint applications to increase adhesion and sub-surface, lateral corrosion if the paint coating is damaged. For pre-paint applications, the coating is generally not sealed.

A variety of cathode materials can be used.... aluminum, stainless steel & lead being the most common. Stainless offers the advantage that the substrate is less susceptible to chemical and electrolytic attack but it offers much lower conductivity and therefore, amp capacity. As a result, it generates heat that the cooling system must dissipate. In today's world, aluminum is far more prevalent and accepted. Some anodizers insist on 6063 alloy as the premier material. However, 6063 is available only in limited extrusion profiles whereas 6061 is available in most any shape and profile. This makes it easier to design cathodes from 6061 and there is minimal difference in the performance. Today, lead has been passed over due to the environmental concerns about its toxicity. This information on cathodes is valid for Type III anodizing as well.

The specification that is most often referred to for this finish is MIL-A-8625 Type II.

**Characteristic of Type II Anodize:**

- Less expensive than other types of anodize with respect to chemicals used, heating, power consumption, and length of time to obtain required thickness.
- More alloys can be finished.
- Harder than chromic anodize.
- More readily dyed with a greater variety of colors and more vibrant results.
- Waste Treatment is easier than chromic anodize, which also helps to reduce cost.

The most commonly used parameters for Type II Sulfuric Acid Anodizing are:

- Sulfuric acid 8-10% b.v. or 12-15% b.w. of 98% concentrated
- Maximum Aluminum Content 8 g/l Desirable  
20 g/l Maximum for Clear Coatings  
12 g/l for Dyed Coatings
- Maximum Copper, Nickel & Manganese Content Combined 40 mg/l Maximum
- Maximum Chloride & Fluoride Content 50-160 mg/l Maximum
- Maximum Iron Content 50 mg/l

• Temperature:	68°F to 72°F
• Agitation:	Moderate Air Agitation
• Filtration:	Optional
• Ventilation	Recommended
• Voltage	Ramp up to 15-24V <sup>Note 1</sup> at 3-5 Volts per Minute
• Amperage	12-15ASF <sup>Note 2</sup>
• Thickness	1.8μ-25.4μ (0.00007"- 0.001")
• Anodizing Rate	Varies with Alloy, Typically 0.000013"/Minute
• Ramp (V/Min.)	5 min from 10V to 18V
• Voltage control	
• Cathodes	carbon steel or 316L SS
• Typical Anodizing Time	Varies with Alloy, Typically 30 to 45 minutes
• Optimum salt spray performance	36 to 336 Hours Depending on Thickness & Seal per ASTM B 117

**Notes**

1. Anodizing based on voltage control is more common than based on current control.
2. The appropriate voltage depends upon the alloy.
3. Because the coating is a dielectric, the current will decrease as the oxide coating forms.
4. Current should be applied within 15 seconds of immersing the part in the anodizing bath
5. Voltage/current is ramped to the desired levels. Typical ramp time is 1 minute.
6. If the dissolved aluminum is below the minimum, you may encounter burning or pitting.
7. Boeing recommends a maximum drying temperature of 140°F.
8. In this author's experience, cathode to anode ratio is not critical

Recommended Voltages:

<u>Alloy</u>	<u>Voltage</u>
1100	15
2011	20
2014	21
2017	21
2024	21
2117	16.5
3003	16
3004	15
5005	15
5050	15
5052	14.5
5056	16
5357	15
6053	15
6061	15
6062	15
6063	15
6151	15
7075	16

Because anodic coatings are relatively thin, the voltage varies relatively little during the process. As a result, most people use voltage to control the Type II process.

## **TYPE III SULFURIC ACID ANODIZING (OFTEN REFERRED TO AS “HARD COAT”)**

Hardcoat anodize is usually done in a sulfuric acid based electrolyte. It is much thicker and denser than the more conventional Type II sulfuric anodize. Hardcoat is often specified for aluminum components subject to high wear applications where superior abrasion resistance is required. It is also used in corrosive environments where a thicker, harder, more durable coating is necessary.

Because the anodic coating is a dielectric, it can also be valuable where enhanced electrical insulation is required.

Since hardcoat anodize can be built up to several thousandths in some cases, it makes this type of anodize a candidate for salvaging worn or mis-machined components.

Hardness will vary with the aluminum alloy and the anodizing parameters. Properly performed, it is typically around 500 Knoop for most of the common wrought alloys. It is generally accepted that the best results occur at 32°F. Proprietary additives can be added that allow the deposition of a hard anodic coating at temperatures up to 50°F and at faster rates.

The proprietary additives are usually based on a Reynolds Aluminum development that was originally called the “MAE Process”. The additives are often a combination of glycolic acid and glycerin. The additives may also allow both decorative Type II and Type III hardcoat to be done in the same solution. It is thought that these additives can interfere with the absorption of the dyes. Therefore, when using the same solution for decorative coatings, it is best to run the additives at the lower concentrations, generally 75% of the recommended for hardcoat applications.

Since there is no standard procedure for hardcoat, commercial results can vary significantly.

### **Characteristic of Type III or Hard Anodize:**

- Improved wear resistance
- Non-conductive
- Can repair worn surfaces on aluminum
- Improve parts surface for slide applications
- Can be black dyed; other colors less decorative
- Finish is harder than tool steel
- Can be ground or lapped

The most commonly used parameters for Type III Sulfuric Acid Anodizing are:

- Sulfuric acid 9-12% b.v. or 13-18% b.w. of 98% concentrated
- Maximum Aluminum Content 5 g/l Desirable  
20 g/l Maximum for Clear Coatings  
12 g/l for Dyed Coatings
- Maximum Copper, Nickel & Manganese Content Combined 40 mg/l Maximum
- Maximum Chloride & Fluoride Content 50-160 mg/l Maximum
- Maximum Iron Content 50 mg/l
- Temperature: 30°F to 32°F<sup>Note 1</sup>
- Agitation: Moderate Air Agitation
- Filtration: Optional
- Ventilation Recommended
- Voltage Ramp up to 75-80V<sup>Note 2</sup> at 3-5 Volts per Minute
- Amperage 24-40ASF<sup>Note 3</sup>



- Thickness 12.7 $\mu$ -115 $\mu$  (0.0005"- 0.0045")
- Anodizing Rate Varies with Alloy, Typically 0.000013"/Minute
- Typical Anodizing Time Varies with Alloy, Typically 30 to 80 Minutes
- Recommended Ramp (V/Min.) 5 min to 25v then continue on up to 45-60 V
- Voltage Control
- Cathodes Aluminum preferred, 316 SS or lead
- Optimum salt spray performance 336 to 3,000 Hours Depending on Thickness & Seal per ASTM B 117
- Optimum hardness Varies with Alloy, up to 500+Knoop for 5052 & 6061

Type III coatings are usually darker in color, typically ranging from green to gray to brown to black depending on the alloy and the thickness.

### Notes

1. Proprietary additives can be added that allow the deposition of a hard anodic coating at temperatures up to 50°F and at faster rates.
2. If the surface area is known, anodizing based on current control is more common than based on voltage control.
3. The appropriate voltage depends upon the alloy.
4. Because the coating is a dielectric, the current will decrease as the oxide coating forms.
5. The anodizing voltages for the alloys follow a similar trend as those above for Type II, only the recommended voltages are higher. That being said, because the anodic coating is thicker, the resistance is always higher and therefore, the fluctuation in voltage is greater. As a result, most people recommend using current density to control the Type III process.
6. It is often recommended to start at 8 volts for 5 minutes, increase to 16 volts for 5 minutes and then adjust the amperage to 24 amps per square foot of surface area.
7. Typically, only dark red or black dyes provide an acceptable finish due to the color of the initial anodic coating. The Type I coating does not readily absorb dyes. Typically, dyeing occurs at higher concentrations of dye, higher temperatures and longer immersion times. It may be helpful to use a dilute nitric dip to open the porosity of the coating; however, this can have a small detrimental effect on the hardness and corrosion resistance of the coating.
8. Boeing recommends a maximum drying temperature of 140°F.
9. In this author's experience, cathode to anode ratio is not critical

## **BORIC/SULFURIC ACID ANODIZING (BSA)**

Boric-Sulfuric Acid Anodize (BSA) was developed by Boeing as an alternative to Type I chromic acid anodizing. Its properties, operating parameters and equipment are very similar to Type II and TSA anodizing.

With the elimination of the hexavalent chromium, this finish environmentally more friendly, increases worker safety and decreases health concerns. Primary applications include aircraft and aerospace components. It is used for corrosion protection and paint adhesion. Paint adhesion is equal or superior to chromic acid, and the process is more energy-efficient than chrome-based processes. Common specifications include It MIL-A-8625, Type I and IC and Boeing's BAC 5632.

### **Boric-Sulfuric Acid Anodize Features:**

- Good for tight tolerance parts: will not change dimensions
- Corrosion protection

- Good for Bonding
- Non-Conductive

The most commonly used parameters for BSA Anodizing are:

- |  |  |
|--|--|
| • Sulfuric acid                              | 30.5 to 52.0 g/l (3 to 5 percent by weight as H <sub>2</sub> SO <sub>4</sub> )     |
| • Boric acid                                 | 5.2 to 10.7 g/l (0.5 to 1.0 percent by weight as H <sub>3</sub> BO <sub>3</sub> )  |
| • Maximum Aluminum Content                   | 5.5 g/l maximum as Al  |
| • Maximum Copper, Nickel & Manganese Content | 237 ppm maximum as Cu  |
| • Maximum Chloride & Fluoride Content        | 0.1 g/l maximum as NaCl  |
| • Chrome                                     | 500 ppm maximum as Cr  |
| • Benzoic acid or Sodium Benzoate            | 1,000 ppm (0.10 percent by weight C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup> ) |
| • Temperature:                               | 76°F to 84°F   |
| • Agitation:                                 | Moderate agitation by air or pumps & eductors                                      |
| • Filtration:                                | Required   |
| • Ventilation                                | Recommended  |
| • Voltage                                    | 16 volts   |
| • Amperage                                   | 10 ASF   |
| • Thickness                                  | 0.2μ - 0.3μ (0.00000787" - (0.0000118")  |
| • Anodizing Rate                             |  |
| • Ramp (V/Min.)                              | 3 to 5   |
| • Voltage control                            | ±1 V   |
| • Typical Anodizing Time                     | 18 to 22 minutes   |
| • Cathode                                    | 304 L or 316L SS, lead or CP titanium (shielded)                                   |
| • Optimum salt spray performance             | 336 hours per ASTM B 117   |

### Notes

1. Anodizing is based on voltage control.
2. Typically, the cathode area may be provided by Type 316L or Type 304L stainless steel anodizing tank. If a nonconductive tank is used, the cathodes can be lead, commercially pure titanium, Types 316L stainless steel, 304L stainless steel or 321 stainless steel cathodes.
3. The cathodes shall have a surface area of not less than one-half the surface area of the work load.
4. Standoff shall be shielding shall ensure that neither the parts nor the rack contact the cathodes during anodizing.
5. The power supply shall be capable of automatically ramping the voltage at the start of the process at a rate of 3 to 5 volts/minute and controlling the required voltage within ± 1 volt.
6. Lower parts into bath with current on, or apply current within 2 minutes after the start of immersion.
7. Obtain 15 ± 1 volts DC with an initial setting of 5 volts maximum and a rate of increase of 5 volts/minutes maximum. Achieve 15 ± 1 volts DC within 7 minutes after application of voltage.
8. Remove parts from anodizing tank within 2 minutes after current is stopped.
9. Rinsing shall commence within 3 minutes maximum after current is stopped.
10. BSA anodizing for pre-paint application is not generally sealed.
11. Work that is not sealed should be painted within 16 hours.
12. Seal Class 1 parts in dilute chromate (0.26 g/l of chromic acid) solution for 23 to 28 minutes at 190°F to 200°F.
13. Final immersion rinse water after anodizing shall be 1000 ppm maximum total dissolved solids (TDS). Control pH of final rinse after anodizing at 2.5 to 8.0. When double immersion rinse is used after anodizing, first rinse shall be 5000 ppm maximum TDS.

14. Boeing recommends a maximum drying temperature of 190°F for non-sealed work and 160°F for sealed work.
15. Benzoic acid or Sodium Benzoate is added to the bath to control organic growth. The solid benzoic acid flakes are sparingly soluble at bath temperature. Therefore, for adds to a bath, the benzoic acid should be dissolved in warm water at a concentration less than 2 g/l. The concentrated solution may be added to the bath as part of makeup water or it may be used as part of the initial bath charge. Processing is not allowed if undissolved flakes are viewable on the surface. Sodium benzoate may be added directly to the bath and it will quickly dissolve.
16. To limit biocontamination growth, sodium benzoate (Section 5b.) can be added to a maximum concentration of 500 ppm (C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup>) by weight in the first rinse of a double counter-current rinse (DCCR) system.
17. Recommended cathode shielding would be perforated PVC sheets with maximum open area

## **TARTARIC/SULFURIC ACID ANODIZING (TSA)**

Tartaric-Sulfuric Acid Anodize (TSA) was developed by Airbus as an alternative to Type I chromic acid anodizing. Its properties, operating parameters and equipment are very similar to Type II and BSA anodizing. To date, its use has not been very prevalent in the United States.

### **Tartaric-Sulfuric Acid Anodize Features:**

- The fatigue strength of the base material is hardly affected.
- High corrosion resistance.
- As a result of the excellent adhesion characteristics, TSA is a suitable pretreatment for further coating processes.
- Small layer thickness (2 to 7 µm), as a result of which dimensional impact is negligible

The most commonly used parameters for TSA Anodizing are:

- |                                       |  |
|---------------------------------------|--|
| • Sulfuric acid                       | 9.6 to 11.7 oz/gal (72 to 88 g/l)      |
| • Tartaric acid                       | 4.8 to 6.6 oz/gal (36 to 50 g/l)       |
| • Maximum Aluminum Content            | 0.7 oz/gal (5 g/l)                     |
| • Copper                              | 50 ppm max.                            |
| • Nickel & Manganese                  | 20 ppm max.                            |
| • Maximum Chloride & Fluoride Content | 25 ppm max,                            |
| • Maximum Iron Content                |  |
| • Temperature:                        | 97°F to 102°F (36°C to 39°C)           |
| • Agitation:                          | Moderate with air or pump & eductors   |
| • Filtration:                         | Recommended                            |
| • Ventilation                         | Required                               |
| • Voltage                             | 18 Volts                               |
| • Amperage                            | 6 to 9 ASF                             |
| • Thickness                           | 0.00008 (2 µm) and 0.0003 (7 µm)       |
| • Typical Anodizing Time              | 24 to 27.5 minutes                     |
| • Anodizing Rate                      |  |
| • Ramp (V/Min.)                       | 2.6 to 3                               |
| • Voltage Control                     | ±1 V                                   |
| • Cathodes                            | 316L SS or lead (shielded)             |
| • Optimum salt spray performance      | 96 hours without seal<br>336 with seal |

## Notes

1. Anodizing is based on voltage control.
2. Used primarily for pre-paint adhesion & sub-surface corrosion resistance. Not used for bonding.
3. Cathodes should be stainless steel or lead with shielding to prevent accidental contact with work.
4. Maximum ratio cathode/anode must be between 1:5 up to 10:1.
5. The bath is subject to organic growth which can be eliminated by heating the bath to 130°F to 150°F (55°C to 65°C) for 5 hours or by UV treatment.
6. Apply current within 1 minute of immersion into TSA bath.
7. Ramp to 14 volts within 4.5 to 5.5 minutes. Hold 14 volts for 19 to 21 minutes. Ramp to 0 volts within 30 seconds to 1 minute. Parts must be removed from the bath within 3 minutes of the end of the DC cycle.
8. Work should be painted within 24 hours of anodizing. Under approved, clean conditions up to 168 hours.
9. Work that is not painted can be sealed in a hexavalent chem film (Alodine 1200), potassium dichromate seal, sodium dichromate seal or chromate seal. Sealing must be done within 4 hours of anodizing.
10. The maximum ratio cathode to anode area must be between 1:5 up to 10:1.
11. Recommended cathode shielding would be perforated PVC sheets with maximum open area

NOTE: FOR ALL SULFURIC BASED ANODIZING PROCESSES, USE AN ELECTRONIC OR HIGH GRADE CONCENTRATED SULFURIC ACID WHICH DOES NOT CONTAIN SIGNIFINCANT CONCENTRATIONS OF IRON OR CHLORIDES.

## PHOSPHORIC ACID ANODIZING

The most commonly used parameters for PAA Anodizing are:

- |  |   |
|--|---|
| • Phosphoric acid                            | 13 to 16 ounces per gallon                  |
| • Maximum Aluminum Content                   |   |
| • Maximum Copper, Nickel & Manganese Content |   |
| • Maximum Chloride & Fluoride Content        | 35 ppm chlorides and 75 ppm fluorides       |
| • Maximum Iron Content                       |   |
| • Temperature:                               | 72°F to 82°F                                |
| • Agitation:                                 | Vigorous Using Air or Pump & Eductors       |
| • Filtration:                                | Recommended                                 |
| • Voltage                                    | 12 to 15 volts                              |
| • Amperage                                   | 3-8 ASF                                     |
| • Thickness                                  | 600 – 2,000 mg per sq.ft. See note 10 below |
| • Anodizing Rate                             | n/a   |
| • Typical Anodizing Time                     | 20 to 25 minutes                            |
| • Ramp (V/Min.)                              | 2 to 7                                      |
| • Voltage control                            | 3%  |
| • Cathodes                                   | 316 SS, lead                                |
| • Optimum salt spray performance             | 336 hours                                   |

## Notes

1. Based on the Boeing specification BAC5555, phosphoric acid anodizing utilizes one of five (5) specified deoxidizers:

- a. FPL Etch
  - b. Henkel Deoxidizer 6
  - c. Chemetall Deoxalume 2310 (discontinued)
  - d. Oakite Deoxidizer 231
  - e. Phosphoric Acid Deoxidizer or PAD (electrolytic)
2. The PAD has the advantage that less rinsing is required between this deoxidizer and the phosphoric acid anodizing tank. It has the disadvantage of being electrolytic; however, the same rectifier can be used for both processes.
  3. The FPL etch and Deoxidizer 6 processes contain hexavalent chromium.
  4. Anodizing is based on voltage control.
  5. Remove the work from anodize solution within 2.5 minutes of turning off the current and rinse.
  6. Time interval from interruption of current to start of rinse shall not exceed 3 minutes for any part of the load.
  7. Water rinse for 5 to 15 minutes, 110 F maximum.
  8. Parts shall be water break-free.
  9. Current density at 15 volts is dependent upon the aluminum alloy, typically 3 to 5 ASF
  10. Maximum 5% AC ripple
  11. The coating is very thin and dense. It cannot be measured by typical procedures. It is generally evaluated visually.
  12. The coating is not sealed.
  13. Bonding must occur within 72 hours of anodizing

## **CONSTANT VOLTAGE vs CONSTANT CURRENT**

Most rectifiers offer controls that allow the unit to output constant voltage or to output constant current. Which is better for anodizing? Most job shops have a variety of work for which they may not know the exact surface area of the part. In this case, they will usually anodize using the constant voltage control. However, if the surface area of the work is known, many anodizers will advocate anodizing using the constant current mode.... or by setting the amps per square foot.... especially for Type III coatings. The consensus is that anodizing at a known current density will provide higher Quality results.

The exceptions would be BSA, TSA and PAA where the aerospace specifications call out for voltage control.

## **ANODIZING RATES.... “RULE OF 720”**

Generally, alloys that respond well to anodizing such as 6061 and 6063 will follow the “Rule of 720,” meaning that it will take 720 amp-minutes to produce a 25- $\mu$ m (1.0-mil) anodic coating thickness on 1 square foot of surface area. The following formula serves as a guide for estimating the anodizing time for the desired coating:

Anodizing time in minutes = (Mils of coating desired  $\times$  720)  $\div$  (current density in ASF)

## **TROUBLESHOOTING THE ANODIZING PROCESS**

Some common problems that occur during anodizing include:

- **Burning** Too high of current density, inadequate racking or contact area, low acid, very high temperature, very low temperature, inadequate agitation, too low of dissolved aluminum. All of these parameters can work together to cause the burning.
- **Thickness variation** Non uniform surface hardness of the substrate caused often by work hardening of the surface during sand blasting, shot peening, buffing. It can also and/or vibratory or mechanical burnishing or polishing. It may also be a result of mixing alloys on a rack, poor electrical contact in inconsistent agitation.
- **Patchy appearance** Inconsistent etching due to inadequate cleaning, silicates remaining on the surface due to inadequate rinsing between soak cleaning and etching &/or inadequate etching leaving oxides on the surface (especially if overheating occurred during machining. Floating oil being dragged into the rinses following any of the cleaning, anodizing and/or dye tanks.
- **Soft coatings** Due to low current density, high temperatures, high acid concentrations &/or an accumulation of the fore mentioned
- **Pitting** Contamination by chlorides, stray &/or galvanic currents due to the galvanic potential between titanium tooling and stainless steel tanks or heating elements.
- **Clarity or Color** As noted, the metallic alloying metals in each individual aluminum alloy will impact the clarity and color of the clear anodic coating. Verify that your alloy is one which will produce a Quality anodic coating.

The impact of common impurities are:

- **Aluminum** Aluminum is dissolved as you anodize. You need dissolved aluminum for Quality results. Too low of aluminum may cause burning. Too high of aluminum may precipitate in the pores and affect the absorption of dyes and the sealing of the coating. The desired concentration of dissolved aluminum varies with each type of anodizing. See parameters above.
- **Maximum Chloride & Fluoride Content** Typically chloride comes from the city water and fluorides from the desmut process. These ions can cause pitting in the aluminum substrate and white spots in the dyed finish. Acceptable concentrations vary but safe numbers, combined for both ions, would be 150 ppm for clear and 50 ppm for dyed work.
- **Iron** Typically iron is dragged in from the ferric sulfate deoxidizer. It can also be found in low grade concentrated sulfuric acid. It reduces the clarity & brightness of the coating, reduces the corrosion protection & reduces the hardness. Acceptable concentrations vary between 50 ppm and 150 ppm but a safe number would be the lower concentration.
- **Copper** Copper can come from the substrate or from the copper busing. Again, acceptable concentrations vary between 50 ppm and 100 ppm but a safe number would be the lower concentration. It will reduce the corrosion protection offered by the anodic coating. Copper will plate out on the cathodes and then often sluffs off to the bottom of the tank. Nickel and manganese have similar effects.

- Phosphates Phosphates can be dragged in from the cleaners, bright dip and/or city water. They do not impact clear anodizing but will interfere with dyeing and sealing at concentrations as low as 5 ppm. So they will impact the color, UV resistance and the corrosion resistance.
- Oil Oil will come in from the cleaning line. It will interfere with dyeing and sealing at concentrations.

## **TOLERANCES**

When trying to maintain part tolerance, you must remember that, as a general rule, the anodizing process builds 50% of the anodic coating into the part and 50% on top of the original surface. As a result, an anodic coating of 0.002” increases the part size 0.001” per side.

## **SHARP CORNERS**

In part design, sharp corners should be avoided. Sharp inside corners can cause the anodic coating on each surface to grow into each other, “crash” and crack, resulting in poor corrosion resistance in the corner. On outside corners, the anodic coating grows away from each other and results in a void and poor corrosion resistance on the edge.

## **RACKING FOR ANODIZING**

When compared to electroplating, designing racking for anodizing is significantly easier for one major reason... since the anodic coating is a dielectric, the coating will build to a very uniform thickness. As the anodic coating forms, the resistance in that area of the part increases and, using Ohm’s Law, which says that current will follow the path of least resistance, the current flows to other areas of the part. As a result, any given part on an anodizing rack has little influence on an adjacent part. Parts can therefore be located more closely together when anodizing than when electroplating. In addition, orientation of the part towards the cathode is of less importance.

Therefore, orientation of the part on the rack basically becomes the simple question of how does it best drain. Unfortunately, since the anodizing tank most often uses air agitation, the opposite question must be asked, how does it capture the least amount of air. Even without air agitation, many of the processes evolve gas which can be trapped. Often, a part that traps solution in one orientation, will trap air in the opposite. Neither situation is tolerable which means that parts must sometimes be rotated during anodizing, turned periodically through the immersion time. Parts can even be processed on a carousel that continually rotates the piece.

Ohms Law brings us to another rule of racking.... avoid mixing alloys on a rack or within a load. Because aluminum is alloyed with different metals, the conductivity of each alloy may differ slightly. If you mix alloys, the more conductive alloy will anodize faster which can lead to inconsistent thicknesses.

Anodizing tooling is most often fabricated from aluminum and/or titanium. Aluminum tooling will be etched through the process and therefore, not last as long. Furthermore, it will itself anodize and since the coating developed is a dielectric, aluminum tooling must be stripped between cycles. Finally, because it will anodize, the area of the tooling will pull current from the rest of the work requiring higher amperages for the load. When using aluminum tooling, it is best to match the alloy of the tooling with the alloy of

the part. Combining all of these factors, aluminum tooling is less expensive to purchase but more expensive to operate. As a result, it is best to use aluminum on tooling for parts with low production capacities but invest in titanium tooling for parts with high production capacities.

Besides cost, the most significant disadvantage to titanium is its conductivity. Aluminum typically conducts about 600 amps per square inch of cross section where as titanium conducts about 34 amps. Insufficient contact area can lead to poor anodizing results due to low current densities. It will increase the heat going into the bath causing a higher demand on the cooling system and finally, can actually burn holes in thin substrate or cause burning in heavier parts. Conductivity is also the reason that stainless steel is seldom used for racking. Stainless conducts about 23 amps per square inch of cross section.

While titanium racks are preferred, they do not offer sufficient conductivity for the electrolytic dyes. It is necessary to use aluminum for two-step anodizing.

Aluminum tooling will anodize and since the anodic coating is a dielectric, it must be stripped between cycles. Stripping can be done in a solution of caustic soda at 5.3 oz/gal (40 g/l) at 105°F (40°C). The alkaline etch tank is often used.

Finally, remember that the tooling must hold the part securely so it is not dislodged by the air agitation and it must provide sufficient contact areas to conduct the current into the part. On the other side of the coin, it must be designed so that the part can be racked and unracked ergonomically with the minimum time and labor.

## **DYING ANODIZED COATINGS**

Because of its relative porous structure, Type II coatings are readily dyed a variety of colors. The dyes are typically either organic or inorganic with the inorganic dyes showing better UV stability. These dyes are typically applied by immersion without any electrical current. Because of the darker color of the initial anodic coating, Type I and Type III coatings are generally only dyed with dark colors.... red or black.

The concentrations of the immersion dyes will vary with different colors but the typical application temperatures are between 130°F to 140°F. Immersion times will vary with the color of the dye with darker colors typically taking longer times. However, typical immersion times are 10 to 15 minutes with saturation occurring at about 20 minutes. The one exception may be black on a hard coat, which could take up to 30 minutes. the dye concentration, the pH of the solution and the temperature are the most important parameters to control.

Type I and Type III coatings often require “activation” by immersing the coating in a dilute nitric acid solution, 1% to 5% at ambient temperatures. Some anodizers advocate the nitric dip for Type II as well. Without activation, the dye may absorb more slowly and cannot reach saturation for the full color to develop.... resulting in lighter colors. With activation, the acid will attack the anodic coating and open up the porosity, allowing the dye to be absorbed more quickly and more thoroughly. On the other side of the coin, opening the porosity will decrease the hardness of the coating. Always a catch-22. These anodized coatings will generally only accept dark dyes.... most commonly black and red.... and then only resulting in lighter shades of the dye.

In recent years, chemical companies have developed dyes with improved UV stability. However, it is generally accepted that the best UV stability is obtained using an electrolytic dye based on tin or stannous



chemistries. This process is often termed “two step” anodizing. The electrolytic dyes are used primarily in the architectural industry and can provide several colors including champagne, gold, brown, bronze and black. The electrolytic dye utilizes an AC power supply. Some applications, typically with large work envelopes, require an initial DC current cycle followed by the AC power cycle.

In summary, the most important parameters to control for Quality results would be water Quality, dye concentration and operating pH. Temperature is not overly critical with low temperature slowing the absorption of the dye and high temperatures causing the sealing process to begin which again inhibits the absorption of the dye. Typically, the temperature for the dyes is between 120°F and 140°F. Time is highly dependent on the color of the dye and the shade that is desired. Longer times promote darker colors and better UV stability. Porosity also impacts time with the tighter pores, for Type I and Type III, require longer times.

## **TROUBLESHOOTING THE DYING PROCESS**

The results obtained from dying can be due to the parameters in not only the dye tank but also the anodizing tank. As a general rule, as the following parameter changes in the anodizing tank, the color in the dye tank will....

Acid Concentration Increase	Deeper
Acid Concentration Decreases	Paler
Dissolved Aluminum Increases	Different Structure
Dissolved Aluminum Decreases	Paler
Current Density Increases	Paler
Current Density Decreases	Deeper
Temperature Increases	Deeper
Temperature Decreases	Paler
Time Increases	Deeper
Time Decreases	Paler
Thickness Increases	Deeper
Thickness Decreases	Paler

When troubleshooting dyes, begin with the water Quality.... calcium, magnesium, iron, chlorides, sulfates all shorten the life of the dye and/or create processing problems. Only quality DI or RO water should be used to make up and replenish the bath.

- Chlorides: Chlorides can cause pitting. Chlorides can come from the water, poor regeneration and rinsing of the ion exchange column &/or a contaminant in inexpensive dyes. Some suggest a maximum concentration of 50 mg/l.
- Iron: Iron as well as several other metals can shift the color of the resulting, dyed finish.
- Aluminum: High levels, above 150 mg/l, can shift the color of the resulting, dyed finish &/or cause a powdery deposit. Fallen parts should be removed.
- Sulfates: High levels, above 1,000 mg/l, can retard the absorption of the dyes by clogging the pores. A dip in to the nitric acid dye activator can counter this effect of sulfates.

- Phosphates: Like sulfates, they can retard the absorption of the dyes by clogging the pores; however, they retard the absorption at lower concentrations, down as low as 5 mg/l.
- Magnesium/Calcium: They can cause a white powdery deposit or white spots on the surface.
- Galvanic Currents: Galvanic or stray currents can cause pitting, especially with dark to black dyes and with magnesium in the alloy substrate. Titanium tooling will enhance this pitting. Hanging a piece of magnesium on to the tooling can help cancel or reduce the galvanic potentials.

Make sure that the rinsing between the anodizing and the dye is adequate to remove the sulfuric acid from the porosity of the coating.... longer immersion times and tempered water will help significantly.

## **ELECTROLYTIC DYING OR “TWO STEP ANODIZING”**

Traditionally, immersion dyes have limited UV stability and will fade with time.... especially with outdoor applications. In recent years, chemical companies have developed dyes with better UV stability. However, it is still generally accepted that the most stable dyes result from electrolytic coloring. As a result, these have become the standard in the architectural industry.

There are some procedures that anodize and color in the same solution. However, these are not readily accepted or common in industry. The most common electrolytic coloring process is performed in a second electrolytic step following anodizing.... thus the term “two step anodizing”.

In this process, tin salts are deposited in the pores to create the color. The more deposition, the darker the color. As a result, one can achieve colors from champagne thru gold to brown, bronze and black.

Of significant note is that this process uses primarily an AC power source of typically 20 volts. For some applications, most frequently when coloring large work envelopes, the power source may initially provide DC power and then followed by AC power.

The basic components of the bath are sulfuric acid, stannous sulfate and a stabilize to inhibit the oxidation of the tin. Some proprietary additives will enhance the color, improve throwing power and provide more consistent deposition over wider current densities ranges for more consistent coloring.

## **SEALING THE ANODIC COATING**

With the following exceptions, the anodized coatings are almost always sealed:

- A non-dyed Type III coating
- A Type II coating used as a pre-paint application
- A PAA deposit used to enhance adhesion of the adhesives during bonding

Sealing improves the light fastness of dyes, prevents leaching of dyes and improves corrosion resistance. However, it also reduces the hardness of the surface.... thus many Type III hardcoat deposits are not sealed unless dyed. Sealing simply “clogs” the porosity within the coating by converting the aluminum hydroxide to a hydrated aluminum oxide. Since sealing dramatically affects the characteristics of the anodic coating, many consider it the most important process step.

There are a number of different types of seals used:

- **Hot DI Water:** Immersion in hot DI water, between 200°F and 212°F at an ideal pH of 6.0, will generate the hydrated aluminum oxide. The typical immersion time is 6 minutes per 0.0001” of anodic coating, resulting in immersion times of up to 45 minutes or more. A hot DI seal, while slow in forming, will work well on clear Type II and Type III coatings; however, on dyed coatings, it can leach the dyes before sealing occurs.
- **Nickel Acetate:** This is the most frequently used seal for Type II and Type III coatings, especially if the coating is dyed. The generic formulation is 5.0-5.8 g/l nickel acetate plus 8 g/l of boric acid operated at 190°F to 210°F at a pH of 5.0 to 5.6. Complete sealing is usually achieved in 10 to 15 minutes, depending on the temperature. The nickel acetate seal will provide superior corrosion resistance versus the hot DI seal. Sometimes, proprietary additives are used with the nickel or cobalt salts to improve the corrosion protection and to provide a superior seal at lower operating temperatures. There is also a lower tendency for smut to form on the work surface.
- **Low Temperature** Low temperature seals, which are generally nickel-fluoride based chemistries, can provide excellent corrosion resistance. Cold sealing is more difficult to control than other formulations and sometimes requires a hot water post-seal rinse to help cure the sealing.
- **Non Nickel Seal** In recent years, seals designed for Type II and Type III coatings have been developed that do not contain nickel. These are typically based on magnesium or cobalt, both non-regulated metal. This development is important because, with the elimination of nickel, there remains no significant concentrations of regulated metals within the anodizing process. This in term, simplifies the waste treatment, often eliminating the need to precipitate, clarify and de-water metals. Depending upon the source, vendors often claim that these seals offer about 90% to 95% of the performance of the nickel acetate seals in terms of UV stability and corrosion protection.
- **Chemeon TCP** While specifically developed as a chem film which does not contain hexavalent chemistries, it has also been found to be an effective seal for Type II and BSA anodizing. In combination with a hot water seal, it has been shown to pass up to 3,000 hours of neutral salt spray resistance in accordance with ASTM B 117 on Type II anodized finishes. It also contains minimal concentrations of regulated metals so, like the magnesium or cobalt based seals, it can eliminate the need to precipitate metals in the waste treatment system.... often requiring only pH neutralization. However, it is also more expensive than most of the other commonly used seals.
- **Dichromate:** The use of a dichromate or chromate seal will provide superior corrosion protection but will also discolor clear and even dyed coatings. These seals typically operate at about 50 g/l at a temperature between 185°F and 190°F.

- **Trivalent:** With the desire to eliminate hexavalent chromium, many companies are now turning towards trivalent chromium seals. The major advantage of these proprietary seals are that they can provide excellent sealing for dyed or clear coatings at ambient temperatures, saving a lot of thermal energy.

The key process parameters are time, temperature and, for the nickel type seals, pH.

- **Temperature:** As a general rule, the hotter the temperature the more complete the seal. Low temperatures can cause smutting.
- **Time:** Sealing time depends on the pore diameter and the thickness of the anodic coating. Sealing starts rapidly and then slows down dramatically. The more porous and the thicker the coating, the longer sealing will take.
- **pH:** For nickel type seals, the pH should be between 5.0 and 5.7. High temperatures can cause the nickel to precipitate, causing the solution to become cloudy and a white to light green powdery deposit that readily wipes off. High and low pH can cause the dyes to bleed out before sealing occurs.

Again, when troubleshooting dyes, begin with the water Quality. Because the seal chemical, whether nickel or chrome, is present in small concentrations, impurities become more active at lower concentrations. Typical maximum concentrations are as follows:

	<b>mg/l</b>
• Phosphates	5
• Silicates	10
• Sulfates	100
• Chlorides	50
• Fluorides	5
• Aluminum	10
• Iron	60
• Heavy Metals	10

Typical issues caused by impurities include:

- **Chlorides** While more tolerant than the anodizing and dyeing process, chlorides can cause pitting
- **Phosphate** Inhibit sealing
- **Sulfates** Inhibit sealing
- **Calcium/Magnesium** Inhibit sealing and can cause a white powder if left on the surface during drying.
- **Silicates** Inhibit sealing
- **Aluminum** White powdery surface

Some typical problem with nickel acetate type seals are:

- **Chalking or Smut** Is often a sign of complete sealing.... the metal hydroxide that is normally deposited in the pores begins to be deposited on the surface of

the work. It is usually non-adherent and easily wipes off. Most proprietary seals have additives to prevent this.

- White Spots White spots &/or streaks can be caused by the precipitation of a variety of contaminants.... calcium and aluminum being the most common but zinc, sulfates and other alloying metals can be the culprit.
- Nickel stains Nickel can precipitate at high pH's in the dye.

For the nickel acetate type seals, filtration is highly recommended.

## **TESTING THE EFFECTIVENESS OF THE SEAL**

Several simple tests are available to evaluate the seal. The most common used today is to use a commercial instrument to test the impedance of the surface. ASTM B-36 offers an accurate dye test that is easily run by immersing the work in 45% nitric acid for 2 minutes, rinsing with DI water, followed by immersion in a solution of 0.5 g/l of blue dye followed by rinsing in DI water. No color should remain on the surface. Salt spray testing by ASTM B-117 or ASTM B-368 is often used to evaluate corrosion protection, which is indicative of a good seal, acceptable anodizing and efficient preparation. Wiping the coating with a white cloth saturated in acetone should not leach any color.

## **MEASURING THE THICKNESS OF THE ANODIC COATING**

The most common method of measuring the anodic coating is with the use of an eddy current thickness tester which is a non-destructive test. These probes are most accurate and provide their highest resolution with a coating that is under 100  $\mu\text{m}$  (4 mils) thick, which is within the expected range of most anodizing applications. These instruments should be calibrated daily with a certified shim that's close to the thickness of the substrate that you are trying to achieve with your coating, and on a surface that's representative of the one you are coating (both in roughness, and alloy). You should not try to measure the coating thickness near an edge.

The anodic coatings can also be measured by coating weight but this method is more time consuming and requires a precise, analytical scale and accurate test coupons.

## **ANODIZING IN BULK OR BASKETS**

It is possible to anodize in a bulk basket to eliminate the labor and cost of individually fixturing the parts.

There are two key factors to being successful:

1. Maintain Cathodic DC Contact Between Parts

As we have noted above, the anodic coating is a dielectric. Therefore, as you make and break DC contact, as would happen in a rotating barrel, the resistance between contact surfaces increases as the coating thickness increases. The most common approach to bulk anodizing is to place the parts within the basket in a tight pack held securely in place by a lid. As a result, bulk anodizing is generally only successful with round parts such as fasteners and rivets. The contact area between these parts is quite small and the resulting contact marks, though visual, are insignificant. Geometries with flat surfaces or that nest together would end up with large unacceptable contact marks.

## 2. Maximize Solution Flow Through the Basket

As we are aware, the characteristics of the anodic coating are heavily influenced by temperature. We also know that as the process proceeds, the heat of rectification increases the temperature of the solution. Therefore, it is critical that the solution flow through the basket be sufficient to dissipate the heat that is generated by the process. Otherwise, the anodic coating will tend to become more porous and softer. You may even find that it will burn or smut. Solution exchange can be difficult because the perforations of the barrel are often moderately small to prevent the parts from escaping the basket or becoming stuck in the holes of the basket. Furthermore, the tight packing of part within the basket tends to inhibit solution flow, especially as you progress towards the center of the basket. In the author's opinion, the best way to assure excellent solution flow through the basket is to have it extend above the solution level with the walls of the basket, above the work solid, without perforations. Solution is then pumped into the top of the basket to create a column of solution above the work to force the solution to flow down through the basket and exit out through the perforations. Again, in the author's opinion, this solution flow down through the basket is more efficient than trying to force solution to flow from the exterior of the basket, via either basket movement or eductors, into the interior.

The basket is generally round and fabricated from titanium. To gain volume, it is better to use a deeper basket in lieu of a larger diameter. The perforations should be as large as the part geometry will allow. The combination of a smaller diameter and larger perforations will allow the DC current to penetrate into the basket at lower voltages and tends to promote a more uniform anodic coating thickness through the basket. As the volume of work increases, the amperage that must flow into the basket will increase. This can often be challenging as titanium is not a very good conductor.... it is typically agreed that it can conduct about 34 amps per square inch of cross section. The performance the basket can be significantly improved if titanium-clad aluminum or copper is used to fabricate the hangers. All of these design features.... small diameter, large perforations and ti-clad hangers.... will also decrease the heat of rectification which in turn leads to better Quality. There is generally a threaded stud that extends up through the center of the basket. This allows the lid to be secured in place with a jam nut to maintain the tight packing of the work. It also allows for the depth of the work within the basket to vary.

## **CHEM FILM or CONVERSION COATINGS**

As noted above, a chem film is applied to aluminum most frequently as a pre-paint treatment to enhance adhesion and to minimize undercoat corrosion should the paint coating be damaged. It can also be used as a stand-alone corrosion treatment and to provide corrosion resistance while maintaining electrical conductivity.

The Mil Spec A-5541 defines two types of chem film.... Type I with hexavalent chromium and Type II with no hexavalent chromium. It also defines two classes.... Class 1A for maximum protection against corrosion, painted or unpainted and Class 3 for protection against corrosion where low electrical resistance is required.

## **SURFACE PREPARATION FOR CHEM FILM**

Surface preparation for chem film is similar to that used for anodizing; however, the chem film is less susceptible to oxides on the surfaces because the hexavalent chromium formulations have the ability to deoxidize the surface. As a result, it is not always necessary to etch the surface prior to chem film. In fact, etching the surface will tend to decrease the corrosion resistance slightly. On the other hand, etching

the surface will provide a more uniform, cosmetic finish. Therefore, many companies will etch when the chem film is not painted and skip the etch when the chem film is painted.

The newer, trivalent chem film formulations are more susceptible to poor cleaning and deoxidizing and should be etched prior to the chem film.

## **OPERATING PARAMETERS FOR CHEM FILM**

The most important parameters for chem film are, in order, immersion time, pH, temperature and concentration. The final three effect the rate of formation which in turn effects the immersion time.

	<u>Reaction Rate</u>
Increase in Ph	Decrease
Decrease in Ph	Increase
Increase in concentration	Increase
Decrease in concentration	Decrease
Increase in temperature	Increase
Decrease in temperature	Decrease
Alloy	Varies with Alloy

If the reaction rate is too fast, the deposit can be powdery and rub off. If it is too slow, the deposit will be too thin and lack color and corrosion resistance.

## **COMMON CONTAMINANTS FOR CHEM FILM**

Common contaminants are:

- Chlorides Chlorides can act as an accelerant. Below 50 mg/l can be beneficial but above 50 mg/l can cause the deposit to form too rapidly and become powdery and non-adherent.
- Sulfates & Fluorides Likewise can act as an accelerant.
- Metals Copper, iron, aluminum and trivalent chromium (in hexavalent formulations) can inhibit and/or prevent deposition and will reduce corrosion resistance.

## **RINSING & DRYING THE CHEM FILM**

Care must be exercised when drying a chem film deposit from a hexavalent formulation. If you immerse in water for too long of time, the chromium can be leached from the deposit. The hotter the temperature, the faster the leaching will occur. Therefore, final rinsing should be for 1 to 2 minutes, especially if the rinse is heated.

When drying in air, you should not heat the deposit to more than 140°F. Overheating can dehydrate the coating.

Both leaching and dehydration will decrease corrosion resistance of the coating.

## **SALT SPRAY PERFORMANCE FOR CHEM FILM**

When properly performed, a hexavalent class 1A coating should provide 185 hours of salt spray when performed per ASTM B 117. A trivalent formulation should provide equivalent performance if not improved performance.

## **CHEM FILMS CONTAINING HEXAVALENT vs. TRIVALENT CHROMIUM**

Traditionally, all chem film formulations contained hexavalent chromium not only in the chemistry, but in the coating as well. It was a key ingredient to provide the Quality corrosion protection that industry sought. As the spotlight fell on hexavalent chromium due to its toxicity, a lot of chemical supply companies have been seeking chemistries void of hexavalent chromium that still provide the performance of the traditional chem film. In most circles, the answer is yes for the Class 3 coating but not yet for the Class 1A coating.

However, while one can argue whether a non-hex chem film is as effective for class 1A coatings as a hex formulation, one cannot argue that more and more industrial firms have qualified at least one trivalent formulation. The product offering the most success to date was pioneered by Chemeon Surface Technologies, Minden, NV ([www.chemeon.com](http://www.chemeon.com)). Their technology has also been licensed to other chemical supply companies.

The Chemeon technology was developed with the US Department of Defense and the US Navy. Initially, these two organizations were among the few to champion the coating and it was added to the Mil-Specs... specifically Mil-Std-5541 and Mil-Std-81706. But as time has progressed, more and more aerospace companies have approved the process. Today, most all major aerospace companies approve it for most of their applications with the notable exception of Boeing. Because the coating is essentially clear, it is difficult to access visually and therefore, Boeing did not approve the process. However, Chemeon will soon release a version that has a blue dye and it is rumored that Boeing will be approving this version.

The basic, active components of the chemistry are The coating consists of fluorides, zirconium in the form of hexafluorozirconate and trivalent chromium operating at a pH of 3 to 4. As the fluorides slight etch the aluminum surface, the pH rises and zirconium and trivalent chromium compounds precipitate with the inner layers being rich in zirconium and the outer layers rich in chromium. The coatings are 90 to 150 nm thick.

In addition to eliminating the toxicity of the hexavalent chromium, other significant advantages include:

- ✓ Because it is very thin, the same coating can meet either Class 1A or Class 3 requirements
- ✓ The coating meets most standard paint adhesion tests.... Specifically FED-STD-141 method 6301.3, "wet tape" and scribe & tape.
- ✓ In excess of 1,000 hours on most all common alloys using neutral salt spray
- ✓ The coating does not require an etch process in the prep cycle which normally consists of a non-etch cleaner, rinse, deoxidizer and rinse. The deoxidizer should be efficient at removing the copper from the aluminum surface but should not be overly aggressive.
- ✓ It operates at ambient temperatures.... 65°F to 120°F
- ✓ During the immersion of work, the solution should not be agitated However, slow solution agitation for good homogeneity within the tank is recommend but this pumping must be stopped prior to immersion. Filtration should not be used.



- ✓ Typical coating weights range from 20 to 45 mg/sq ft. Since the coating is essentially clear, this is a common means of Quality control.
- ✓ As coated, it offers better abrasion resistance
- ✓ The coating can handle higher temperatures.... up to 350°F
- ✓ Waste treatment costs are minimal as often, the rinse waters can be discharged to a POTW (sewer) with only pH adjustment.

One characteristic that most people will point out.... a trivalent formulation requires more care and attention to detail in order to be successful.... in both preparation of the substrate and in control of the bath.

## **NON-CYANIDE BASED CHEM FILMS**

In the original formulations, potassium ferricyanide was used as an accelerator. Unfortunately, this is a very stable compound that is difficult to treat and untreatable with conventional, sodium hypophosphate systems. Fortunately, there are newer formulations that have eliminated the cyanide-based accelerators that still offer the excellent corrosion resistance of the original formulations; they are, however, slightly more difficult to operate because they require tighter chemical controls.

## **ELECTROPLATING ON ALUMINUM**

We briefly touched on electroplating aluminum above by stating that the aluminum must first be coated with another, less reactive metal generally using either an immersion coating or an electroless deposited coating. These processes are in themselves relatively complicated and would deserve multiple pages of description and information. Therefore, this article will not cover these processes or the subsequent electroplating the aluminum.

## **ELECTROLYTIC DEPOSITION OF ALUMINUM**

Due to the galvanic or electromotive series, aluminum cannot be electroplated from aqueous solutions since the redox reactions will favor the breakdown of water into oxygen and hydrogen. Therefore, it is only possible to electroplate aluminum from non-aqueous solutions using solvents within a noble atmosphere free of oxygen. In a nutshell, it is generally too expensive and difficult to be a commercially viable process.

## **BASIC EQUIPMENT REQUIREMENTS FOR ALUMINUM FINISHING**

As with each of the above topics, one could probably write a book on the equipment requirements. But as a summary, here is a summary of the basic requirements:

- **Tank Construction**  
Today, the most common material of construction for tanks is polypropylene. However, polypropylene does not handle acidic, oxidizing environments particularly well. As a result, tanks for Type I anodizing, hexavalent chem film and certain deoxidizer chemistries might better be fabricated from PVC, polyethylene or, depending on the process, stainless steel. PVDF is an excellent choice but unfortunately, its cost is often prohibitive.

Temperature will also be a limiting factor for plastic tanks. As a general rule, polyethylene and PVC should not be used for tanks heated above 120°F and polypropylene for tanks above about 175°F. These temperatures are conservative and will vary depending on the design of the structural support for the tank (i.e. girthing). But it should be remembered that these plastics lose structural strength as the temperatures increase.

For higher temperatures, it is usually best to fabricate tanks from mild steel or stainless steel where the chemistries allow. However, many of the alkaline chemistries become excellent paint strippers at elevated temperatures and attack or streak the paint on the exterior of mild steel tanks. Therefore, for cosmetics, it is often best to use stainless steel. If the tank is insulated, a good compromise is to use steel for the tank and stainless steel for the sheathing of the insulation.

At the other end of the temperature range, it is best to fabricate the Type III anodizing tanks which are operating as low as 30°F with CoPP... a polymer of polyethylene and polypropylene. This plastic becomes less brittle at these temperatures than polypropylene or PVC.

For either plastic, polypropylene or PVC, it would be recommended to use heat-bent corners, butt fusion welding and extrusion welding for tanks greater than 48" deep or 120" long. These manufacturing techniques result in a far more robust fabrication. Heat bent corners are as the name implies... continuous corners in which the plastic is heated and then bent around a mandrel. Butt fusion welding machine heat the entire edge of the plastic and then hydraulically force the edges together to provide fusion through the entire depth of the weld. Extrusion welding uses a gun that is capable of extruding a single weld bead that is up to ¾" wide.

- **Exhaust Ventilation**

In today litigious society, it is recommended that all chemistry and heated tanks have exhaust ventilation. Proper ventilation reduces the corrosion and improves the environment for the worker's health. As a minimum, the alkaline etch and anodizing tanks should be exhausted.

While lateral hoods, located between tanks, are significantly more efficient at capturing the process vapors, a push/pull ventilation system, with hoods located behind the tank and push air directed toward the hood, is the least expensive way to ventilate the tanks. If the distance from the front of the tank to the hoods exceeds about 10 feet or if the work can significantly block the push air, strong consideration should be given to using lateral hoods.

As noted above, the bright dip process requires special considerations to control the NO<sub>x</sub> that the process generates.

- **Agitation**

Agitation of the chemistries is important to assure:

- Uniform chemical concentration within the tank
- Replenishment of chemistry at the boundary layer of the part (immediately adjacent to the surface of the part)
- Uniform temperature within the tank
- Dissipate heat generated at the surface of the part

Air agitation is the most economical method of agitation or stirring the solution. However, it also generates a lot of aerosol misting as the bubbles break the surface. This aerosol misting creates a corrosive atmosphere for equipment in the vicinity of the tank rim, dissipate a lot of thermal heat and increases chemistry consumption. All of these factors increase the operating cost of the process as well as increases maintenance costs to keep the line clean and repair corrosion damage.

As a result, it is recommended that solution agitation using pumps and eductors be used in chemistry and heated tanks. Pumps should be sized to provide 4 to 6 tank volume turnovers per hour. Eductors can be used to enhance solution flow at the workpiece and reduce the size of the pumps. An eductor is a venturi device that enhances the flow by a factor of 4X to 5X depending on the pressure provided the eductor.

Care should be taken in designing the eductor discharge manifolds. Solution leaves the eductor at a high velocity but at a narrow angle, about 30° or 15° per side. The result is that you can get hot spots.... areas of high and low agitation.... if the eductors are orientated directly at the work and from close distances.

While it is better to use solution agitation in chemistry tanks, two exceptions might be ferric sulfate based deoxidizer and the anodizing tank. The ferric deoxidizer requires air agitation to keep the iron oxidized to the ferric ion state. Most anodizers will say that air in the anodizing tank is required to quickly dissipate heat generated at the part surface.

Ideally, when air is used, the discharge sparger should be located so that they rise close to but without hitting the work. This will minimize the possibility of trapped air and dislodging work from the fixture.

The air must be clean and free of oil. Some try to use compressed air that has been filtered but even if clean, this usually produces poor results. The uniformity and degree of air agitation is difficult to control with the high pressures.

- **Rectification**

The Quality of the DC current, in terms of AC ripple, is subject to differing opinions by experts for any of the anodizing processes. The consensus is that none are overly sensitive to AC ripple. Traditional SCR thyristor units will produce less than 5% AC ripple at full rated output; however, as the voltage of amperage fall off, these units can produce significantly higher AC ripple. They can often exceed 50% at low DC outputs.

Switchmode power supplies offer a lot of advantages, beginning with their AC output. They will be less than 2% AC ripple across their entire output range. They also offer better control of the DC output.... typically providing  $\pm 1-2\%$  control of the full output amperage and  $\pm 3-5\%$  of the full output voltage. Finally, they are significantly smaller and have better electrical efficiency and power factor.

Many people feel that water cooled power supplies are more reliable and offer greater long term service. This can be especially true if the units are located in a dirty or corrosive environment. Water cooling does add more cost for smaller units, especially when considering the requirement for tempered water, plumbing and pumping. However, for large units, the units themselves will be more cost efficient. It should be noted that the cooling water must be tempered.... heated to maintain the water temperature above the dew point. Should the water temperature drop below the dew point, there is the possibility of condensation within the unit which can cause significant damage.

Typical voltage and amperage requirements are:

- |            |         |           |
|------------|---------|-----------|
| ○ Type I   | 42-48V  | 5-10 ASF  |
| ○ Type II  | 18-24V  | 15-24 ASF |
| ○ Type III | 75-100V | 25-50 ASF |

- BSA                      10-15V                      15-20 ASF
- TSA                      10-15V                      15-20 ASF
- PAA                      12-15V                      15-20 ASF

It should be noted that the required power or voltage will vary with parameters such as anode-to-cathode distance, electrolyte concentration, temperature and racking. The required amperage will vary primarily with part geometry, racking orientation, anode-to-cathode distance and racking. Typical anode-to-cathode distances are 6” to 10”.

- **Busing**

Busing is required to conduct the current to the tank.... specifically, the cathodes and the anodizing fixture.

The busing must be sized to handle the amperage without generating heat.... heat increases the resistance in the circuit and requires greater voltages. DC current flows through the entire cross section of the metal where as AC current flows on the surface. Therefore, in calculating the current capacity, we use the entire cross section of the metal bar.

When designing busing, or tooling for that matter, the following conductivities can be used:

- Copper                      1,000 amps per square inch of cross section
- Aluminum                      600 amps per square inch of cross section
- Steel                      120 amps per square inch of cross section
- Titanium                      34 amps per square inch of cross section
- Stainless steel                      23 amps per square inch of cross section

Cabling is often used because it is less expensive to install. It must be a multi-stranded cable so that it can easily bend for installation. One of the challenges of using cabling is how to properly size the cable. Many ampacity charts are based on AC current rather than DC current. Therefore, determining the capacity of the cable for DC current may not be easily done. Additionally, ampacity charts are calculated for cabling that is run individually and in the open. In anodizing facilities, the cabling is often bundled or run in raceways. Therefore, be conservative in sizing the cable and use between 60% to 75% of the rated capacity as found on most ampacity charts.

Solid copper or aluminum bus is used for installations with higher amperage capacities.

Many designers will emphasize that both the front and back of the tank should be bussed and that the busing should ideally be of equal length. This results in excessive busing costs. Equivalent results can be obtained by busing the end of the tank closest to the power supply and simply over sizing the busing. Because the anodizing process builds a dielectric coating, the resistance of the coating will tend to cause uniform coating thickness. Therefore, the small resistance change from one end of the tank to the other has a minor influence on the uniformity of the coating itself.

When designing the busing on the top of the tank, it is highly recommended to use aluminum bar instead of copper. While both will be attacked by the chemistries, when copper dissolves into the process tank, it will inevitably be a contaminant with disruptive effects occurring at significantly lower concentrations than aluminum. That being said, tank-top busing from either metal should be protected from chemistry dripping from the work as it enters and exits the tank. Protection can be done by plastisol coating, wrapping with platers tape and or covering the bus with PVC piping that is cut in half.

A copper-based, conductive grease should be applied to all connections within the busing circuit. This grease will inhibit corrosion in the joint which in turn will minimize resistance.

- **Cathodes**

Cathodes can be fabricated from a variety of materials..... aluminum, stainless steel and lead being the most common. Lead has fallen out of favor due to its toxicity and lack of fabrication sources. Aluminum is used most often for Type II and Type III. 6063 alloy is favored but only available in a limited number of extruded shapes. 6061 alloy is acceptable, available in many shapes and performs nearly as well as 6063. Stainless is used most often for BSA, TSA and PAA. Stainless has a significantly lower current carrying capacity so it will generate heat that must be dissipated by the chilled water system. Stainless carries about 23 amps per square inch of cross section while aluminum carries about 600 amps.

Ideally, the cathodes should be conformed to the work envelope, stopping about 4-6” above the bottom of the work envelope and inside the ends of the work envelope. Many anodizers neglect the top of the work but the cathodes should be shielded down to 4” below the top of the work envelope. Some specifications require that the cathodes have shielding to prevent short circuiting by accidental contact with the work. Finally, shielding at the solution interface will minimize the corrosion of the cathode in this area.

While there are many references to the work to cathode ratio, in practice it does not have a significant impact on the Quality of the anodized coating.

Aluminum cathodes in sulfuric acid anodizing baths will last longer is a small cathodic potential is applied during downtime. Aluminum with a cathodic charge will not dissolve in the sulfuric acid. This cathodic charge need only be about a half to one volt. Keep in mind that this DC circuit requires an anodic surface in the tank!

- **Heating**

Type I, BSA and TSA require operation at an elevated temperature.... typically 100°F to 130°F for Type I and 80°F to 85°F BSA and TSA. However, the soak cleaner, etch, dyes and seal typically require even greater heat. Typical operating temperatures are:

- Alkaline Soak 140-160°F
- Acid Cleaner/Etch 100-120°F
- Alkaline Etch 100-140°F
- Immersion Dyes 135-145°F
- Non-nickel seals 175-185°F
- Nickel seals 195-200°F

With low ambient temperatures, it is often beneficial to heat the Type II tank. Without heat, it is often necessary to “dummy” the tank in the morning to bring the temperature above 68°F.

Tanks are generally heated with electric immersion heaters, steam or pressurized hot water. Of these methods, electric immersion heaters require the least capital investment while pressurized hot water provides the most efficient operational expense.

Electric immersion heaters mounted within polypropylene or PVC tanks does present a fire safety issue unless installed properly. All installations should include the following methods of safety:

1. The heaters have a cold zone that extends to at least 3” below the operating the operating solution level.
2. Heaters remain at least 2” from the nearest tank wall.

3. A non-resettable thermal fuse in the cold zone that will melt if the heater reaches unsafe temperatures.
4. A level sensor that will shut off power should the solution fall to unsafe levels.

Heating coils for Type II may be fabricated from PVDF, Teflon, zirconium and/or occasionally 316 SS. Stainless should be used only for hot water heating and should be grounded to avoid corrosion by-polar currents.

- **Cooling**

Most of the anodizing processes operate within a fairly tight temperature range. As current flows through the electrolyte, heat will be generated. In addition, heat may be generated at the cathode as well as at the work surface. Therefore, all anodizing tanks should have a cooling system to dissipate the heat of rectification and good, aggressive agitation to assure that the temperature is consistent throughout the tank and to dissipate the heat from the work surface and heat exchanger.

The heat of rectification is calculated by the following formula: Volts x Amps x 3.412 = Btus/Hr

Often, with large rectifiers, it can be difficult to provide enough heat exchange area with in-tank cooling coils. If in-tank coils are used, it is preferable to locate them out from behind the cathodes, perhaps on the front &/or back tank walls and/or floor of the tank. If located on the tank floor, the coil should be protected with a perforated PVC sheet to prevent damage from falling parts.

With large rectifiers, it is often necessary to use an external plate and frame heat exchanger. While often more efficient, this arrangement does require a pump and pumping the electrolyte outside of the tank. In-tank coils should be grounded to minimize stray or bi-polar currents.

Note that variation in the temperature of any anodizing process will impact the characteristics of the coating.... primarily the porosity which in turn impacts the hardness, wear resistance and ability to absorb dyes. Close temperature control is essential for Quality anodizing results. It also requires excellent agitation to carry the heat quickly away from the part surface.

Cooling coils are most frequently fabricated from 316 stainless steel and should be grounded to avoid corrosion by-polar currents. Stainless coils will corrode slowly but are generally the first choice since plastic coils have poor heat transfer qualities and zirconium &/or niobium coils are very expensive.

- **Material Handling**

Moving racks through the process steps can be done manually or with the assistance of material handling.... either a “free fall” or “guided fall” hoists.

A free fall hoist is one in which the work is suspended from a wire rope or chain. These hoists include monorails or bridge cranes. Generally the vertical lift is motorized while the horizontal motion can be either manual or motorized. The limitation of these hoists would be that they are subject to swing and sway as they start and stop. This motion eliminates the possibility of automation, slows production throughput and requires larger hoist clearances and tanks.

With a guided fall hoist, the vertical lift is stabilized by tracks or guides to eliminate or minimize the swing and sway. As a result, these hoists can often be automated. They include sidearm, overhead and rim-runner designs. They are capable of moving very large work envelopes. A sidearm hoist is a cantilevered design that runs along the backside of the tanks to lift loads of 50–

250 lbs. Overhead hoists can handle larger loads from 250 to 4,000 lbs. Rim-runner designs have capacities similar to the overhead and use rails typically located within 30” of the tank rim. They are most often used in applications where headroom is limited.

Moving racks manually limits the size of the work envelope. Typically, operators can only move racks that weigh 35 pounds or less and are 30” tall or less.

- **Automation**

Automating the process line provides the most reliable results for the anodizing process. All parameters can be monitored and computer-controlled, eliminating human error.

Rectifiers can be automatically set using part information stored in a database, and process control information can be saved to files for generating reports showing process times, operating conditions of each process, system alarms, etc. Statistical process-control analysis can be included to monitor and analyze data to improve product and process quality.

The control system can make chemical additions, log amp-hours, and signal maintenance routines. Touchscreen terminals allow easy operator access to process information, set-points and load status.

Loads can be processed by a fixed timeway cycle, running the same process repeatedly, or by a random loading cycle, which runs an unlimited product mix. Fixed timeway operation provides maximum machine throughput, while random loading provides maximum flexibility.

## **BASIC WASTE TREATMENT FOR ALUMINUM FINISHING**

Again, much can be written but the following is a summary. If regulated metals are present in the finishing process, then it will likely be necessary to remove these metals from the wastes prior to discharge to the sewer. Regulated metals and their allowable discharge limits may vary by locale but the common, regulated metals for finishing aluminum are copper, zinc, chromium and nickel. If these metals are present, it will likely be necessary to use a removal methodology prior to discharge to the sewer. Copper and zinc are present only in the aluminum substrate. Unless there is significant etching, these metals do not generally exceed discharge levels. Chromium can be present in the deoxidizer, Type I anodizing, chem film, dyes and chromate or dichromate seals. Nickel is present only in the nickel acetate seal.

On occasion, locales can have limits on Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) that come into play. If the TDS limit is exceeded, the most common method of compliance is ion exchange. If the TSS limit is exceeded, the most common method of compliance is filtration.

### **Batch vs. Continuous Flow**

Batch treatment offers the advantage that the capital equipment is less expensive and you can test prior to discharge so compliance is more robust. However, most anodizing facilities produce too much rinse waste for batch treatment.

### **Rinse Waste vs. Concentrated Waste**

The wastes generated by the rinses is generally very dilute and thus, readily treated by pH neutralization, precipitation or ion exchange. However, the wastes generated by dumping or diluting the process chemistries or by regeneration of ion exchange resins are significantly more concentrated than the rinse

wastes and therefore, potentially disruptive to a continuous flow treatment system, whether precipitation or ion exchange. Concentrated wastes should be either batch treated or bled slowly through the continuous flow precipitation system. If there are no significant concentrations of regulated metals, they can be bled through the pH neutralization system. They should not be treated by ion exchange or RO.

### **pH Neutralization**

If there is no nickel in the seal or chromium in the process, then the wastes can often be treated by a simple pH neutralization system to assure compliance to pH discharge limits which are generally pH 6 to 9.

### **Chemical Precipitation**

If regulated metals are present, then the waste may need to be treated by chemical precipitation of the metals, usually as the metal hydroxide. The precipitation then has to be clarified or removed from the waste stream, typically by gravity separation, and then dewatered, typically by filter press.

If hexavalent chromium is present, it would have to be reduced to the trivalent in order to be precipitated as the metal hydroxide.

This precipitation process is the most expensive step, in labor and waste disposal costs, involved in the treatment of wastes from an aluminum finishing process.

This might be a good place to mention the benefit of seals that do not utilize regulated, heavy metal.... the most common being nickel and/or chromium. By eliminating these metals, it is often possible to eliminate the need to precipitate and clarify the metals. As noted above, this is the most expensive step and, regrettably, the resulting metal hydroxide sludge is composed primarily of aluminum and, depending on the deoxidizer used, iron.... both metals that can generally be discharged legally to the sewer.

The elimination of regulated metals in the sealing process is often not possible due to the requirements of many aerospace or other industry specifications. However, in recent years, seals based on magnesium or cobalt have been developed and available from several vendors. These seals can often be used for Type II and Type III processes with corrosion and UV stability results that approach, but regrettably, not exceed those of the traditionally used nickel acetate seals. Depending upon the source, vendors often claim that these non-nickel seals perform at 90% to 95% of the nickel seals in terms of corrosion resistance and UV stability.

With the elimination of the nickel and chrome, the only other regulated metals that might be found in the effluent from an anodizing process would be the copper and/or zinc from the aluminum substrate. With the typical etch times and rates, these metals are generally found at levels below their discharge limits. However, with high etch rates, with aluminum alloys high in these metals and/or with discharge limits below the standard Federal limits, it can be possible to exceed the legal discharge limits.

### **Ion Exchange**

Properly applied, ion exchange has been very successful in a number of locations in purifying and recycling the dilute rinse waters from an aluminum finishing facility. IX can often be used to recycle up to 80% of the water used.

### **Membrane Treatments or Reverse Osmosis**

There are a number of membrane treatments.... ultrafiltration, nanofiltration and etcetera. Typically, these membrane systems are more successful used for water pretreatment of the incoming water source than as a waste treatment methodology. When used for waste treatment, the membranes often foul and



the reject waters are not concentrated enough to make off-site disposal economic and thus, require further treatment. Fouling can be especially troublesome due to the nature of the aluminum precipitant.