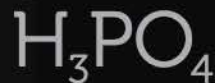




BRIGHT DIPPING ALUMINUM



TECHNICAL INFORMATION BULLETIN

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1101 Skokie Blvd., Northbrook, IL 60062

TABLE OF CONTENTS

Introduction.....	1	Rinsing.....	27
Technical Assistance.....	1	Number and Configuration of Rinses	27
Additional Information.....	1	Types of Rinses	28
Mechanical Finishing	2	Drain Time.....	29
Buffing.....	2	Rack Design, Size, and Shape of Parts	29
Optimizing Conditions.....	2	Recovery of Phosphoric Acid	29
Buffing Problems	4	Construction of Rinse Water Recovery System	30
Cleaning.....	5	Design Pointers.....	30
Alkaline Cleaners.....	5	Operating Pointer	31
Acid Cleaners	6	Additional Information.....	31
PCS Sales Phosphoric Acid Cleaner	6	Anodizing.....	32
Control of Cleaning Baths.....	7	Mechanism of Coating Formation	32
Analysis of PCS Sales 342-AC Acid Cleaner	8	Parameters Affecting Anodizing.....	33
Bright Dipping	9	Control of Anodizing Baths.....	34
Mechanism.....	9	Anodizing Problems	34
PCS Sales DAB Products	10	Determination of "Free" Sulfuric Acid in	
NOx (Nitrogen Dioxide) Fume Scrubber.....	11	Aluminum Anodizing Baths	35
Neutralizing a New 316L Stainless		Sealing.....	37
Steel Tank / Liner / Coil	11	Nickel Acetate Pre-Seal.....	37
Starting a New Bright Dipping Bath	12	Preparation of Nickel Acetate Pre-Seal.....	38
Operation and Control of		Hot Water Seal	39
the Aluminum Bright Dip.....	13	Nickel Acetate Seal.....	39
Recommended Operating Parameters		Seal Problems	40
for Bright Dipping.....	14		
Effects of Major Variables	15		
PCS Sales Phosbrite® Products.....	16		
Operation of a Phosbrite® Bath	16		
Safety and Handling	17		
Phosphoric Acid Storage System	17		
Aluminum Alloy.....	18		
Procedure for Analyzing the Bright Dip Bath	19		
Measurement of Specific Gravity.....	19		
Water Addition Chart	20		
Determination of Nitric Acid.....	22		
Nitric Acid Addition Chart.....	24		
Determination of Aluminum Concentration.....	25		

TABLES AND FIGURES

Tables

Table 1	
Operating Parameters of PCS Sales	
Acid Cleaner 342-AC	7
Table 2	
DAB Bright Dip Bath Composition	9
Table 3	
Recommended Operating Parameters	
for Bright Dipping	14
Table 4	
Effects of Major Variables	15
Table 5	
Recommended Operating Parameters	
for Phosbrite	16
Table 6	
Water Addition Chart	
(Specific Gravity Correction)	20
Table 7	
Nitric Acid Addition Chart	24
Table 8	
Parameters Affecting Anodizing	33
Table 9	
Recommended Operating Parameters	
for the Nickel Acetate Pre-Seal	38
Table 10	
Hot Water Seal Process Conditions	39
Table 11	
Nickel Acetate Seal Process Conditions	40
Table 12	
Maximum Limits of Contaminants	43

Figures

Figure 1	
Bright Dipping Reaction Mechanism	10
Figure 2	
Recommended Operating Range	14
Figure 3	
Schematic of Typical Phosphoric	
Acid Storage System	17
Figure 4	
Counter-Current Rinsing	27
Figure 5	
Water Savings with Counter-Current Rinsing	28
Figure 6	
Spray and Immersion Rinse	
Combination	29
Figure 7	
Mechanism of Anodic Coating	
Formation	32
Figure 8	
Relationship Between Specific	
Gravity, Free Sulfuric Acid and Aluminum	
Content of Anodizing Baths	36

INTRODUCTION

The phosphoric acid/nitric acid chemical polishing bath (Bright Dip) is widely used to produce specular finishes on a variety of aluminum alloys used for automotive, lighting, appliance and architectural trim. Consistent production of a high quality finish requires a thorough understanding of the Bright Dip bath and its function, as well as careful control of the entire finishing process. This process manual addresses all phases of the bright aluminum finishing process, including pretreatments as well as the anodizing and sealing steps required to protect the bright finish.

Mechanical finishing may be used to provide a variety of surface textures of aluminum. For bright trim, buffing is required to remove surface scratches, rolling marks and die lines, thus providing a surface which is free of surface defects. A properly designed and operated cleaning cycle is required to remove all lubricants, buffing compounds and surface oxides which would interfere with the brightening process. The Bright Dip bath functions by leveling the microscopic roughness of the aluminum surface, thus reducing the amount of light which is scattered and increasing the specularity of the surface. After Bright Dipping, most finishers utilize a sulfuric acid anodizing process to produce a clear, protective oxide coating on the metal surface. That oxide coating is then partially converted to an insoluble, hydrated alumina which closes the coating's microscopic pores and protects it from corrosion. Bright Dipping Aluminum discusses the function of each of these process steps, and outlines the control requirements for each.

TECHNICAL ASSISTANCE

Combining the individual finishing steps to produce an integrated bright anodizing system frequently results in a system with additional, highly specific process requirements not discussed in this manual. This is particularly true when other types of finishes are produced by the same system. Recognizing that individual process requirements exist, PCS Sales maintains a Technical Service Staff which can assist in tailoring any portion of the bright anodizing process to individual requirements. Technical Service Representatives are available to assist in determining the cause of finishing problems, and to develop specific modifications to prevent their recurrence.

ADDITIONAL INFORMATION

Bright Dipping Aluminum provides insight into many of the requirements of producing high quality bright anodized aluminum. While this is as complete as possible, all requirements and potential problems could not be addressed. Therefore the recommendations contained herein must be evaluated and applied by a competent, well-trained staff.

Because all chemicals used in bright anodizing present health and safety hazards, every person assigned to work where they are used or stored must be instructed in their hazards and in their proper handling. The manufacturer of each chemical should be contacted to obtain complete handling, health and safety information.

Material safety data bulletins are available for all of PCS Sales' cleaners and specially formulated phosphoric acids for Bright Dipping. Material safety data bulletins, storage and handling information or other technical assistance may be obtained by contacting PCS Sales Customer Service.

MECHANICAL FINISHING

Mechanical finishing refers to operations which alter the surface and appearance of an aluminum part by physical means such as grinding, polishing, buffing, shot blasting or tumbling. The main objectives of these processes are to (1) remove metal surface irregularities and imperfections in order to smooth the metal surface or (2) apply a texture to the surface of the part. The method and extent to which mechanical finishing is used will depend upon the initial state of the metal surface, the method of manufacture of the article and the finish desired.

There are five types of wheel grinding and polishing operations commonly used on aluminum:

- 1) Texture or Scratch Brushing
- 2) Grinding
- 3) Roughing
- 4) Polishing
- 5) Buffing

Although all of these operations may be used by bright anodizers to some extent, buffing is the most frequently used type of mechanical finishing.

Buffing

Buffing is used to remove minor scratches and die lines and to increase the specularity of the aluminum part. It is as much an art as a science since the skill and experience of the operator play a significant role in the final results. The buffer must strike a balance between the quality and the cost of the finish by tailoring buffing sequences and materials to the alloy, shape, and surface condition of the part. Although prior experience is invaluable in tailoring the process conditions to the part, following a few basic guidelines can minimize buffing problems and rejection due to improper buffing.

Finishing begins the moment raw materials are received in the plant. Material handling, storage, tools and press practice all may affect both the buffing operation and the final appearance of the part. Further, the best of buffing procedures and techniques can be completely negated by careless handling after buffing. Freshly buffed surfaces should be protected against fingerprint corrosion by wiping them with a whiting compound such as calcium carbonate. In addition, buffed parts should be carefully racked on suitable trays to prevent traffic damage.

Optimizing Conditions

In the mechanical finishing of aluminum it is best to use only buffing operations and to avoid polishing whenever possible. The coarse abrasives of the polishing belts cause scratch patterns which are extremely difficult to remove with subsequent buffing. This becomes even more significant in the finishing of long sections where all work is unidirectional.

If uniform chemical treatment is to be accomplished, all preexisting oxide must be removed and removed uniformly. A common error is to under-buff. Many times the parts appear visually "clean" or bright after buffing, yet show defects after Bright Dipping. Tests have shown superior coloring results when a caustic treatment is added between cutting and coloring. Although this sequence may not be economical, it does point out the need for adequate oxide removal.

Pressure

The contact pressure of the buff on the work piece is as important as the selection of compound and buff material, and must be determined empirically for each part. Excessive contact pressure will distort the buff and cause uneven wear and an inferior surface finish. Furthermore, buffs under excessive pressure do not retain the compound which does the cutting or coloring. The wheel is simply a soft cloth acting as a carrier for the compound, and cutting action does not come from the contact of the cloth on the metal. High contact pressures are also a cause of rapid heat buildup on the work. Temperatures beyond 400°F/204°C can cause metallurgical changes in the aluminum and can cause cloudiness of the anodic coating in the areas where overheating occurred. Other factors which affect temperature are the buff material, degree of ventilation, and thread count of cloth.

Compound Application

The application of compound to the buff is a critical operation. Beyond the optimum amount, additional compound will not increase metal removal. Excess compound results in the buildup of residues on the parts which are often difficult to remove. As a rule, excessive compound is applied when compound is applied infrequently; the wheel then has either too much or too little material at any given time. At low compound levels there is little metal removal. At high compound levels too much compound is deposited on the work. Ideally, the compound should be applied frequently in small amounts to minimize deviation from the optimum.

Speed

A peripheral wheel speed of 7000 ft./min. has been found most desirable for buffing aluminum. This is an average speed and some adjustment based on part configuration and size is necessary.

The direction of part travel in relation to buff rotation has an effect on surface condition. Considerably more cutting occurs when the part is passed opposing or “against” wheel rotation than when the part is passed complementing or with wheel rotation. Preferable cutting and coloring should be done in the same direction and with the rotation of the wheel to prevent skip and drag. For best results, cutting and coloring should be accomplished using different compounds and wheels.

Alloy

Metal selection has an effect on the surface obtained after buffing and bright anodizing. Harder metals with finer grain size give best results. In addition, they tend to be more “ding” resistant during subsequent handling. For best results, the hardest material temper compatible with required formability should be utilized in fabricating the part.

Buffing Compounds

An abrasive material is the significant ingredient of either solid or liquid buffing compounds. A bar of buffing compound is a cutting material (abrasive) held together by bonding agents such as greases, stearic acid, and waxes. The abrasive material may also be formulated as a water emulsion of oils to make the composite sprayable. Automatic multiple station buffing operations will normally use liquid compounds. Bar compound use is restricted to hand operations. For a compound to be effective it must be tenacious enough to adhere to the wheel, but this is the same property which makes a part difficult to clean prior to bright anodizing. By working with suppliers and on-the-job testing, the proper binder can be chosen.

The abrasive most commonly used is tripoli, a naturally occurring material composed primarily of amorphous silica with up to 5 percent iron oxide. Iron oxide is responsible for the reddish color, and increasing amounts of iron oxide deepen the color. Tripoli is the most widely used buffing compound

for aluminum finishing because of its availability and low cost. However, there is the potential hazard of iron oxide retention on the surface of the buffed piece. The iron oxide is not apparent after buffing, and is probably chemically bonded to the surface. If not removed with a mild-etching cleaner, the particles may cause dull or lightly pitted areas during Bright Dipping.

White amorphous silica, an iron-free abrasive, is occasionally used for color buffing aluminum. This substance is quite soft, however, and accomplishes little cutting. A third abrasive, aluminum oxide (Al_2O_3), is very hard and has good cutting and coloring properties. Formulations containing this abrasive are more costly than the others. However, where metal removal and surface contamination are critical, it may be less expensive in the long run. In a multiple station buffing sequence (cut and color), alumina should be used for the coloring stations.

Buffing Pads and Wheels

A great many buff types are available and they, too, should be tailored to the job. Again, vendors' recommendations and shop testing determine the best buff type for a particular operation.

The most common buffs are bias-cut muslin. Their buffing performance is determined by thread count, number of piles and number of folds around the circumference. For the hard buffing or cutting operations, a wheel of high thread density (86–93) and large number of folds (No. 8 bias) might be used. For coloring a low thread density (64–68) and few folds (No. 2 bias) should be used.

Since heat is a problem in buffing aluminum, the buffs must be designed and constructed to dissipate heat rapidly. The color buffing wheel must have good shedding ability. That is, it must throw off metal particles and compound, otherwise the face will become "solid" and gouging will occur on the metal surface. The buffs must then be "raked" to remove the hard facing.

Buffing Problems

Pitting

If the buffing compound is driven into the aluminum surface due to excessive pressure, a pit will result. The pit may not be apparent after buffing, or even after cleaning, but will show up after Bright Dipping.

Mottling

Elevated aluminum surface temperatures during buffing may be caused by excessive pressure, friction due to lack of lubrication, or hard buffs. Surface temperatures above 400°F / 204°C can cause metallurgical changes in the aluminum which appear in the anodized part as gray areas. No defect will be apparent until after Bright Dipping or anodizing.

Cloudiness

Areas on parts which have been "double" buffed, i.e., buffed more heavily than the rest of the part due to overlap in buffing from both directions, may appear cloudy after Bright Dipping. Cloudiness may also be due to inadequate or incomplete cleaning of the buffed surface. A compound which resists cleaning can be formed due to the reaction between aluminum and the stearates in the binder. This compound can be removed only in an etching bath, either with an etching alkaline cleaner or a caustic etch.

CLEANING

Metal cleaning is a broad term covering the preparation of metal surfaces for an infinite variety of finishing processes. In the aluminum industry, a prerequisite for the success of nearly every finishing system is a clean surface. While the choice of the cleaning method for aluminum is determined by a number of factors, the most important considerations are: type of contaminant to be removed, surface condition required for subsequent finishing and size and shape of parts to be cleaned.

The soils prevalent on aluminum are usually fairly easy to remove. Because of the ease of working aluminum, drawing and machining lubricants need not be of the types that are very resistant to cleaning. The somewhat unique soil on aluminum sheet of marking inks and buffing compounds represents the most difficult soils to be removed. Several other contaminants are found. Among the most common ones are oil, grease, wax, or protective films remaining after rolling, drawing, extruding, and fabricating operations. Shop dust, mill scale, and metal oxides are some other contaminants that may also be present and must be taken into consideration.

Cleaning has been said to be the most common operation performed in the transformation of aluminum from raw metal to the finished product. Its importance, therefore, cannot be overemphasized. Many a costly anodizing job has been rejected because of improper or inadequate cleaning. Careful attention to cleaning will go a long way toward avoiding expensive rejections and ensuring a quality product.

The problems relating to the cleaning of aluminum are not simple, largely because of the sensitivity of the metal and its reactivity with many commonly used cleaners. Most aluminum finishers use alkaline cleaners or acid cleaners, separately or together in various combinations.

Alkaline Cleaners

Alkaline cleaners are used to remove drawing and stamping oils and buffing binders. They are also used where heavy soil loads are encountered. The cleaning ability of an alkaline cleaner comes from its ability to saponify fatty acids and fats and emulsify other oils and greases. Additives in the alkaline cleaners enable them to wet soils and to keep them suspended or dissolved.

Formulations of effective cleaners also contain water softeners which sequester or chelate calcium and magnesium salts in hard water to minimize the possibility of insoluble soap formation. They also contain buffering agents, which enable the cleaning solution to maintain a constant pH where its cleaning action is most effective.

Even mildly alkaline cleaners will attack aluminum, particularly at higher temperatures unless an inhibitor is present. Sometimes a slight attack causes an etched appearance which is not objectionable, but is usually not desirable for bright work. Inhibitors are sometimes incorporated into the cleaner to reduce or prevent this etching in the cleaning stage. The most commonly used cleaner inhibitors, sodium silicate and sodium chromate, are not suitable for use on the bright anodize line.

Silicated cleaners, operated in the pH range 11.3–11.7, protect the aluminum by forming a thin surface film. If this is not removed completely in hot cleaner rinses, upon entering any acid bath (an acid cleaner, Bright Dip or anodize bath), the silicate is converted to silicic acid which is insoluble. The insoluble silicic acid adheres to the parts and may cause pitting or an uneven, streaked appearance.

Chromate inhibited cleaners are usually operated at a pH of 10 or less. They are not as effective as silicate cleaners, and the chromate disposal problem has all but eliminated their use in anodizing.

Other compounds may be used to give alkalinity and at the same time not be as harsh on the aluminum base metal. Such systems are preferred in the operation of the Bright Dip line to avoid the silicate contamination and chromate disposal problems. These other systems may contain sodium carbonates, sodium phosphates, sodium metaborates, or sodium tetraborate (borax). Frequently two or more these are blended together to maintain a reasonably high pH upon the addition of acid soils. These may also be blended as buffers with sodium hydroxide to overcome the hygroscopic nature of sodium hydroxide and make for easier mixing and handling.

Acid Cleaners

The major advantages of using an acid cleaner are: (1) better metal oxide removal in an acid cleaner — these oxides include aluminum oxide and magnesium oxide which may be present due to in-plant corrosion or even rolled into the metal upon forming; (2) chlorinated and viscous paraffin oils are more easily emulsified in an acid cleaner — these oils are often used in the stamping and forming operations; (3) embedded buffing abrasives are more easily removed in an acid cleaner; and (4) any other residues remaining after other cleaning operations are removed. The metal surface is termed “activated”; that is, the surface is free from any surface films and pure base metal is presented to the next operation. The ideal cleaning cycle then should have, as a final cleaning step, an acid cleaner. The acid cleaner could follow an alkaline cleaning stage or may be used by itself if the soil load is not too heavy.

These types of acid cleaners are in use in the anodizing industry today:

- (1) Phosphoric acid cleaners like PCS Sales 342-AC are superior for removing buffing compounds and metal oxides. In addition the surface is left “activated” or oxide free, which produces superior bright work.
- (2) Sulfuric acid cleaners require inhibitors to prevent the parts from being deeply etched. Without tight control, parts may be dulled by these cleaners.
- (3) Citric acid cleaners use a very mild acid as their base. They do not have the cleaning power of phosphoric acid cleaners, nor do they leave the surface etched or “activated” for further processing. They are used in areas where phosphate restrictions prohibit the use of phosphoric acid cleaners.

PCS Sales Phosphoric Acid Cleaner

PCS Sales offers a phosphoric acid based cleaner: 342-AC. This cleaner is designed for the removal of ground-in, caked-on buffing compounds and drawing oils from drawn, stamped or extruded aluminum parts. It will also remove some heat and water marks which are normally carried through conventional alkaline or neutral cleaners. When operated in the recommended ranges shown in Table 1, this cleaner leaves the aluminum parts slightly frosted. This frosting, unlike that produced in a caustic etch, will not reduce the brightening or smoothing action of the Bright Dip. In fact, parts will brighten or etch more uniformly because the surface is “activated” and pure base metal, rather than a heavy oxide film, is presented to the next treatment bath.

PCS Sales 342-AC is designed as a second-stage cleaner following an alkaline cleaner, although it may be used as a single-stage cleaner where the soil load is light. This formulation is superior for the removal of caked-on, ground-in buffing compound, and will leave the aluminum surface “activated” for subsequent Bright Dip or etch operations.

Table 1: Operating Parameters of PCS Sales Acid Cleaner 342-AC

Cloud Point (°F)	95 minimum
Temperature (°F)	95–180
Time (min.)	1–5
Concentration (% by vol.)	8–9
pH	1.5–3.5

Control of Cleaning Baths

The chemical control of cleaning baths will vary with the type of cleaner and time allotted for laboratory control. These controls are usually supplied by the manufacturer of the chemicals and are based on extensive experience.

The tests usually used to analyze aluminum cleaners are as follows:

- (1) Emulsion cleaners — break the emulsion with acid and measure the solvent separation.
- (2) Etching, buffered alkaline cleaners and silicated cleaners — titrate with standard acid solutions.
- (3) Acid cleaners — titrate with standard base.
- (4) High detergent cleaners — detergent titrations, surface tension, acid–base titrations, cloud point determinations or surfactant analysis.
- (5) Water Break Test — The simple water break test remains the most widely used method, in shop practice, to test for cleanliness. A cleaned metal panel, after being submerged in cold, clean, clear water, would show a continuous film of water over the entire surface. The presence of any residues will cause the water film to break, leaving those areas not wetted. Sometimes small areas will fail to show up immediately with this test, so sufficient time should be allowed to ensure that the film is continuous over the entire surface.

The control procedure used for each cleaner should be specified by the manufacturer of the cleaners.

“How long will a cleaner last?” is a common question. Since soil load, drag-out of solution and type of soil are different for each operation, this is difficult to determine without a production test. Cleaners which etch usually require more maintenance than the non-etching cleaner. The quality of the part produced and the number of rejects attributed to poor cleaning are the real measures of a cleaner’s value.

The preparation of metals for finishing is a most important consideration and, therefore, the cleaning operations require a considerable amount of planning. The appearance and acceptability of the finished part depends primarily on a sound cleaning process and clean foundation for the finish. A properly designed cycle will result in a quality part; likewise, an improper cleaning cycle will lead to rejects and higher costs. Therefore, the importance of proper cleaning cannot be overemphasized.

Analysis of PCS Sales 342-AC Acid Cleaner

Reagents Required:

- | | |
|---|---|
| 1. Sodium Hydroxide Solution | 0.5 N |
| 2. Indicator Solution (Bromphenol Blue) | Dissolve 0.1 g Bromphenol Blue (Fisher Scientific Co.) in 7.1 ml of .02 N Sodium Hydroxide and dilute to 250 ml with distilled water. |

Apparatus Required:

1. 250 ml Erlenmeyer flask
2. 10 ml burette
3. 10 ml pipet

Procedure:

1. Pipet 10 ml of the acid cleaner solution into the 250 ml Erlenmeyer flask.
2. Add about 40 ml of water and 2–3 drops of the indicator.
3. Titrate with the 0.5 N NaOH to the end point (change from greenish yellow to the first distinct blue or pH 4.5).

Calculation:

% cleaner (by volume) = ml of 0.5 N NaOH x 0.92

BRIGHT DIPPING

Bright Dipping is a process for increasing the specularity or brightness of aluminum by leveling the microscopic roughness or “peaks and valleys” on the surface of aluminum parts. The application for Bright Dipping is somewhat limited because it does little macropolishing or smoothing of scratches or pits. This limitation underscores the need for proper buffing and careful handling prior to Bright Dipping.

There are two primary Bright Dipping formulations — DAB and Phosbrite. DAB Bright Dip products consist primarily of phosphoric and nitric acids with additives to reduce nitrogen dioxide fumes and enhance the brightening ability of the bath. Phosbrite products are phosphoric, nitric and sulfuric acids with similar additives.

The range of typical operating conditions for DAB Bright Dip baths is shown in Table 2. Phosbrite operating conditions will be addressed later on page 14.

TABLE 2: DAB Bright Dip Bath Composition

Phosphoric Acid	70–82%, by weight
Water	15–22%
Nitric Acid	2–5%
Dissolved Aluminum	15–50 g/L
Additives	Less than 1%
Temperature	190–220°F/88–104°C

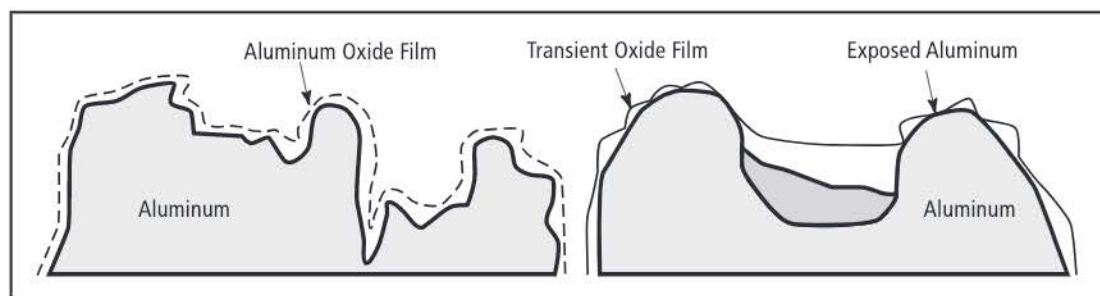
Mechanism

The surface of an aluminum part can be visualized as a series of “peaks and valleys” or high and low areas. For the Bright Dip bath to smooth this surface, there must be a faster rate of attack and more metal removed at the “peaks” than in the “valleys.”

When aluminum is placed in a hot Bright Dip solution composed of phosphoric and nitric acids, the nitric acid reacts with the aluminum to form an aluminum oxide film. This film is immediately dissolved by the phosphoric acid, as shown in Figure 1.

These reactions occur more rapidly at the peaks than in the valleys because the Bright Dip solution is very viscous. There is less agitation in the valleys than at the peaks; therefore, the rate of the reaction in the valleys decreases as the solution becomes saturated with aluminum phosphate and the nitric acid is depleted.

FIGURE 1: Bright Dipping Reaction Mechanism



The Bright Dip bath must be carefully balanced to obtain the optimum amount of metal removal. For a given smooth, buffed piece, the maximum brightness will occur when the minimum amount of metal necessary to get beneath the buffing marks is removed. More metal removal will decrease the image clarity. This is because the brightening activity proceeds along the grain boundaries and can result in orange peel, or a bumpy, wavy effect.

Please refer to PCS's "Bright Dipping Aluminum" Technical Bulletin for complete information and step-by-step Bright Dipping instructions. It may be obtained by visiting our website at www.nutrien.com or by contacting your account manager.

PCS Sales DAB Products

PCS Sales DAB 80 and DAB 85 solutions for Bright Dipping can be formulated to contain any or all of the following additives: 1. Copper Metallic Brightener 2. Fume Suppressant

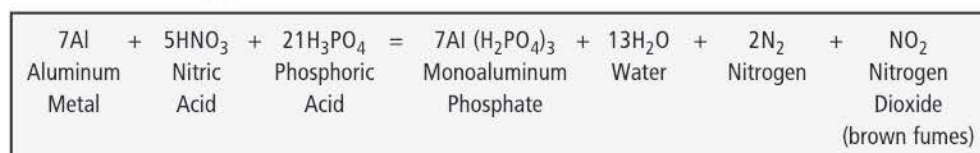
Metallic Brightener

The preferential attack of the Bright Dip at the peaks is enhanced by the copper metallic brightener in PCS Sales Bright Dip acids. During Bright Dipping, a galvanic cell is set up between aluminum and copper. The copper will plate out on the aluminum surface. This film of copper, like the film of aluminum oxide, forms and dissolves faster at the peaks than in the valleys. The film plated in the valleys protects that aluminum from further attack as shown in Figure 1. By using PCS Sales Bright Dip products, the maximum brightness is obtained with minimum metal removal.

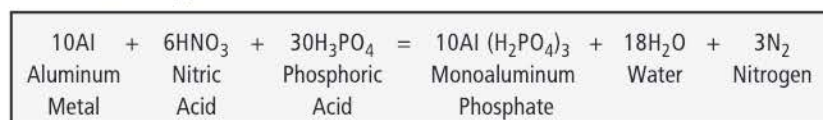
Fume Suppressant

The fume suppressant in PCS Sales phosphoric acids reduces the amount of the irritating, red NO_x fumes produced from the reaction of nitric acid and aluminum and reduces the amount of nitric acid consumed. The following reactions illustrate the effects of a fume suppressant.

Without Fume Suppressant:



With Fume Suppressant:



NOx (Nitrogen Dioxide) Fume Scrubber

Aluminum Bright Dip applications recommend an exhaust hood design and *require* a specialized fume scrubber. It is recommended to isolate the Bright Dip tank and first rinse after Bright Dip within the anodizing line. To achieve this, a completely enclosed area can be designed. This design should encompass both the Bright Dip Tank and the first rinse tank.

A specialized fume scrubber is required to effectively eliminate the Nitrogen Dioxide (NOx) fumes generated. During the dipping process, as aluminum is immersed in the Bright Dip tank, a powerful evolution of brown/orange gases evolves very quickly. This off gassing of NOx fumes continues during the immersion process. The enclosure (mentioned above) must be designed to effectively capture the fumes emitted during the aluminum parts immersion in the Bright Dip as well as travel to the first rinse.

After the immersion process is completed and the process rack is lifted from the Bright Dip solution and moved to the first rinse tank, the off gassing of NOx *ABOVE* the tank surface area is at its peak. Therefore there must be effective exhaust above the tank surface area to capture these gasses during rack transfer. The exhaust volumes to the Bright Dip scrubber must be exactly calculated to capture all of the NOx gases. A standard acid scrubber cannot achieve the required capture of NOx emissions. Only a specifically designed scrubber for NOx fumes will enable zero visible emissions from the Aluminum Bright Dip process.

The NOx fume scrubber *design* is critical. Federal and/or State regulations will not tolerate NOx exhaust to the atmosphere at a rate greater than regulated opacity. The Bright Dip scrubber parameters are all larger and greater than that of a standard acid scrubber. The Bright Dip fume scrubber is designed much larger in diameter for additional resonance time, with approximately 3 times the packing height, and a required recirculation/irrigation rate onto the scrubber packing 3-4 times greater than a standard acid scrubber. Irrigation reagents are required additions to the NOx fume scrubber for oxidation of NO and de-oxidation of the NOx.

Neutralizing a New 316L Stainless Steel Tank / Liner / Coil

Before beginning the operation of an aluminum Bright Dip, the bath, liner and all coils must first be neutralized against the leaching of heavy metals. The following procedure should be followed for any new or replacement items that will come in contact with DAB and/or Phosbrite products. This applies to all 316L SS tanks including the first rinse tank after Bright Dip if it is constructed of 316L Stainless Steel:

- Add water to within 10" of bath top
- Turn on air for 2 hours
- Empty tank to ½ full
- Add nitric acid to 30% by volume

Bring bath to full with water – NO AIR...NO HEAT

- Allow tank to sit for 24-48 hours – NO AIR...NO HEAT
- Empty to storage / waste treatment

Begin Bright Dip start-up procedure.

Starting a New Bright Dip Bath

Discussion

When starting up a new bath, two problems are very likely to occur unless certain precautions are observed. These problems are known as *transfer etch* and *orange peel*. Transfer etch is easy to recognize in that it will be most prominent on the leading edges of the parts and primarily on work at the top of the rack. Parts which tend to hold heat, such as heavy extrusions, are the most severely affected. Orange peel is the term given to work that exhibits a general roughness.

Both transfer etch and orange peel may be caused by the initial high activity of a new Bright Dip bath. This high activity or rate of attack of a new bath may be attributed to the lack of dissolved aluminum which acts as an inhibitor. Thus, as the aluminum content of a bath increases the activity decreases. A bath with no aluminum will have a rate of attack at least twice that of a bath with 50 grams/liter of aluminum. For the aforementioned reasons, PCS suggests an initial aluminum concentration of 35 g/L. The aluminum concentration will equilibrate with time based on your operating conditions. The other parameters will have to be balanced around the stabilized aluminum concentration.

Two other ways in which the activity of a Bright Dip bath may be decreased depend on temperature and nitric acid concentration. Lowering the temperature of the bath from 210°F to 190°F decreases the rate of attack by about 21%. Lowering the nitric acid concentration also decreases the rate of attack. By dropping the nitric content of a new bath from 3% to 2%, a 14% decrease in rate of attack is affected.

Procedure

Fill the operating tank up to normal operating volume (at least 2-3 feet away from the top of the tank) with Bright Dip solution.

Add 2% nitric acid (HNO_3) by weight to the operating tank. Although the addition of nitric acid reduces the dissolution rate of aluminum, it also helps to prevent corrosion of the operating tank itself.

Bring the bath temperature to 195°F.

Begin air agitation and start adding alumina trihydrate to the Bright Dip bath. Add alumina trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) at 84 pounds per 100 gallons of Bright Dip solution to achieve a concentration of 35 g/L aluminum. Alumina trihydrate is a pure source of aluminum and will go into solution rapidly. The alumina trihydrate is 31% water and although increasing aluminum concentration increases the specific gravity, the water acts to reduce the specific gravity of the bath.

Note:

The dissolution of aluminum or alumina trihydrate will cause the evolution of gas and temporarily increase the **volume** and **temperature** of the bath.

Alumina Trihydrate may be purchased from any chemical supplier.

Make a slurry with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and H_2O . (The slurry will go into solution easier than adding just the powdered $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.)

After the alumina has dissolved, check the nitric acid concentration and specific gravity. Maintain a nitric acid concentration of at least 2% by weight. Increase the temperature to 220°F and continue air agitation until the desired specific gravity has been attained.

Bring the temperature down to 205 - 210°F. Add Bright Dip until reaching operating volume and bring the nitric acid concentration up to 3.0% by weight. Re-check the specific gravity, check the aluminum concentration and commence operation.

During production, the nitric acid concentration and specific gravity should be checked at least every 4 hours. For most uniform results, make small, frequent additions of nitric acid. Aluminum concentration may be checked weekly or monthly. Only virgin Bright Dip should be added to maintain tank volume.

Operation and Control of the Aluminum Bright Dip

The Bright Dip bath must be carefully balanced and maintained to produce the maximum brightness possible. As the bath is operated, the bath composition changes due to the following:

1. Nitric Acid Reaction (reduces acid content)
2. Water Boil Off (reduces water content and increases specific gravity)
3. Nitric Acid Boil Off (reduces nitric acid content)
4. Aluminum dissolution (increases aluminum content)

Drag-out on the parts removes total solution but does not change the actual composition of the bath. However, the addition of makeup solution containing no aluminum reduces the aluminum content.

The aluminum Bright Dip bath can be controlled very simply by adopting the following daily operating procedures. Methods of analysis for specific gravity, nitric acid, and aluminum are discussed in "Procedure for Analyzing the Bright Dip Bath" on page 19.

1. Add DAB solutions to maintain level in the tank. Any one addition should not exceed 5% by volume of the Bright Dip solution.

Stainless steel tanks, coils and heaters rely on the presence of nitric acid to prevent corrosive attack, so the nitric acid content should not be allowed to drop below 2%.

2. Add nitric acid on a regular schedule to maintain a preestablished operating range. Only 42° Baume ~67% nitric acid should be used to avoid an excessive drop in the specific gravity of the bath. Any one addition of nitric acid should not exceed 1/2% by volume (preferably 1/4%) of the Bright Dip solution. A nitric analysis should be made at least once per shift (and preferably twice), and the schedule of nitric additions modified as necessary to maintain the correct range (see Table 7, p. 24).
3. Add water on a regular schedule to maintain a preestablished specific gravity range. A specific gravity measurement should be made at least once a shift (and preferably twice), and the schedule of water additions modified accordingly (see Table 6, pp. 20-21). Water is also lost overnight by evaporation, therefore it is recommended that a "blanket" of water, usually 1/2 to 1 inch, be added to the bath at the close of work to prevent precipitation of aluminum phosphate ("ice").

To add a "water blanket" to the Bright Dip bath, **turn off the air agitation** in the bath and let the surface settle. Then simply allow clean water from a hose or other source to gently flow across the surface of the bath until a "blanket" of 1/2 -2 inches of water is formed depending on the length of down time for the bath ... less water = shorter down time. It must be uniform across the top of the bath. It is not necessary to turn off the heat to the bath but you may turn it down to 160-180°F. Remember to check the specific gravity at start up and adjust for any extra water.

4. The aluminum content usually stabilizes under the given set of operating conditions but should be checked about once a week. For a fresh bath, the increase in aluminum due to dissolution exceeds the loss of aluminum due to drag-out. Thus, the aluminum content of the bath increases. Higher aluminum contents, however, slow down the rate of dissolution and increase the drag-out of aluminum (due to higher content of aluminum in the solution and higher viscosity). Eventually, the increase in aluminum by dissolution is offset by the loss of aluminum by drag-out, and the aluminum content becomes stabilized.

The above schedule of control procedures should work very well if the physical operating conditions (time of immersion, temperature, agitation, and transfer time) are kept constant during each operating shift. Changes in any of the foregoing will produce a change in the additions required to keep the bath in balance, as will a change in the number or shape of parts on the rack.

The ranges recommended in Table 3 and Figure 2 are based on average operating conditions and represent best practice under such conditions for DAB baths. However, conditions quite different from normal may be encountered in actual practice. In particular, the alloy and physical characteristics of the aluminum may require alteration in operating conditions from those given.

TABLE 3: Recommended Operating Parameters for Bright Dipping with DAB¹

Aluminum Content ¹ , g/L	20	30	40	50
Specific Gravity at 80°F/27°C				
Maximum	1.71	1.72	1.73	1.74
Minimum	1.69	1.70	1.71	1.72
Nitric Acid Content (as % HNO ₃ by wt.)	2.4–2.6	2.7–2.9	3.0–3.2	3.3–3.6
Temperature °F	190–195	195–200	205–210	215–220
Temperature °C	88–90	90–93	96–99	102–104
Time, Minutes	1–2	1 1/4 to 2 1/2	1 1/3 to 3	2–4
Agitation	Vigorous air combined with mechanical agitation is preferred			

Notes:

1. Bright Dip operating parameters should be selected based on aluminum content.

FIGURE 2: Recommended Operating Range for DAB

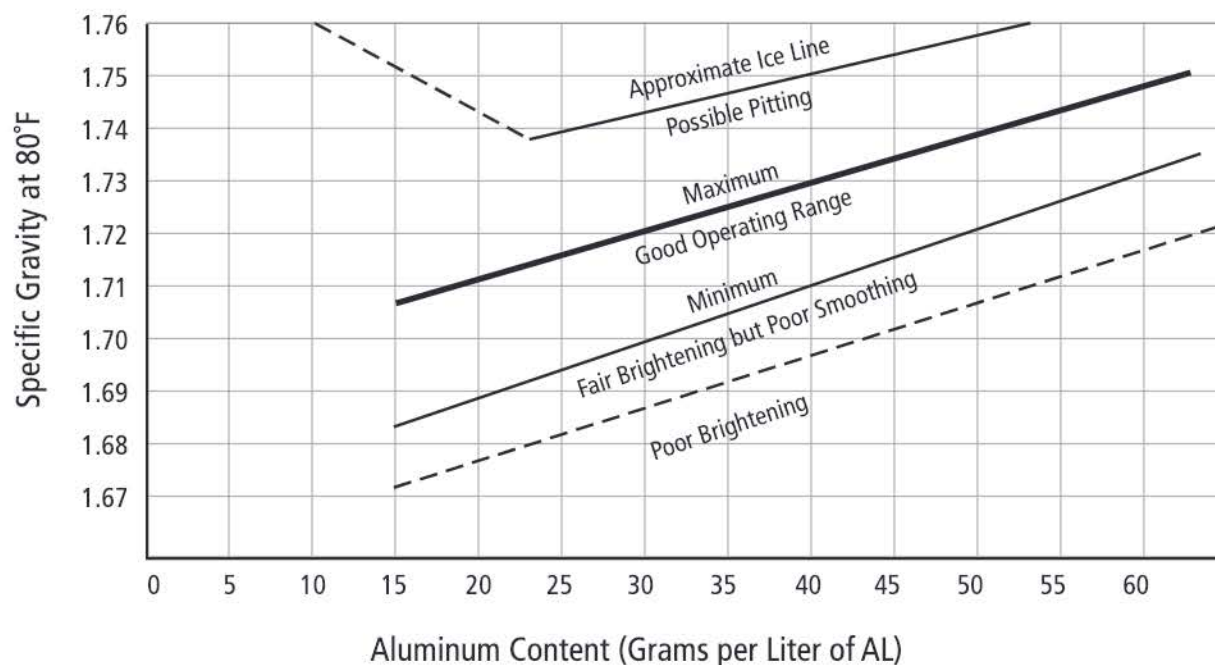


TABLE 4: Effects of Major Variables

The effects of the major variables of the Bright Dip bath on smoothness and the rate of metal removal (brightness) are explained in the following table:

Variable	Rate of Metal Removal	Smoothing Action
Temp., °F/°C	Increases approx. 5% for each 5°F/3°C except for a leveling out effect between 195°F/90°C and 205°F/96°C, but above 205°F/96°C the increase in rate becomes linear again.	Maximum smoothing action appears to occur at end of leveling out somewhere between 195°F/90°C and 205°F/96°C
Time, min.	First 5–10 seconds quite rapid, then rate becomes linear with time.	Maximum smoothness usually occurs at point of minimum metal removal necessary to get under surface blemishes but before grain boundary lines are emphasized.
Agitation	Where agitation is not sufficient to renew the surface solution rapidly, the rate of attack may be reduced (and pitting tendencies may be enhanced) by as much as one-half.	The more agitation the better the smoothness. Insufficient agitation can lead to pitting and gassing marks.
Transfer Time	Attack continues until parts are cooled down.	Parts may be etched due to the continuing reaction of Bright Dip, or the Bright Dip solution may dry on the hot parts leaving white streaks along the top edge (transfer etch).
Nitric Acid Content, as % HNO ₃ by wt.	Addition of nitric acid reduces the rate of attack of pure phosphoric acid until a certain min. concentration. Beyond this point (about 1% HNO ₃ for a bath containing 40 g/L of Al) an increase of 1/4% HNO ₃ increases rate of attack approximately 3%.	Smoothing action decreases with increasing nitric (above 1%). However, pitting tendency is greater at lower nitric contents. Best nitric level is the lowest concentration that does not produce pitting, but not lower than 2%.
Water Content, as % H ₂ O by wt.	If water content is higher than the solution crystallization point, rate of metal removal increases approximately 10% for each 1% increase in water content.	Smoothing action decreases with water content. Max. smoothing action occurs just below crystallization point or point of "low-water" pitting.
Aluminum Content, as g/L of Al (80°F/60°F)	Rate of metal removal decreases rapidly with increasing aluminum content. At 45 g/L the rate of metal removal is less than 1/4 that at zero aluminum content (other factors being constant).	Increasing aluminum content does not change smoothing action. However, importance of agitation becomes more critical and at high aluminum contents enough agitation to renew solution at the surface becomes almost impossible.
Phosphoric Acid, % by wt. (DAB)	Because the amount of phosphoric acid, 70–82%, is so high, small changes in phosphoric acid content have little effect on the rate of metal removal.	Phosphoric acid is used to maintain the high viscosity and specific gravity necessary to selectively dissolve the aluminum at the "peaks."

PCS Sales Phosbrite® Products

PCS Sales PB 172 and 174 are phosphoric acid-sulfuric acid-nitric acid solutions which were developed in the 1950s. Throughout the years the formulations have been modified to address the technological improvements which have occurred in the aluminum brightening industry. Both Phosbrite 172 and 174 are unique formulations for superior chemical polishing of aluminum and offer several advantages over conventional phosphoric acid-nitric acid solutions (DAB). Phosbrite advantages include:

1. Increased specular reflectance on a wide range of alloys.
2. Removal of fine scratches and other imperfections.
3. Greater tolerance for soil contamination without producing contamination pits.
4. Wide operating parameters.
5. Elimination of transfer etch.
6. Lower emission of fumes than similar processes containing nitric acid and sulfuric acid.

Operation of a Phosbrite® Bath

The operation and control of a Phosbrite bath is similar to a conventional DAB bath. The most significant change is the specific gravity at which the bath operates.

TABLE 5: Recommended Operating Parameters for Phosbrite

Aluminum Content, g/L	15	30	45
Specific Gravity at 80°F			
Maximum	1.79	1.80	1.81
Minimum	1.76	1.76	1.76
Nitric Acid, % by wt.	3.5–4.5	3.0–4.0	2.5–3.5
Temperature, °F	205–220	205–220	205–220
Temperature, °C	96–104	96–104	96–104
Time, min.	1.5–4.5	1.5–4.5	1.5–4.5

Fresh Phosbrite is added to the Bright Dip tank as necessary to maintain tank working volume (replacement of drag-out losses). The only other necessary operating additions are nitric acid and water. As with the previously described DAB Bright Dipping bath, the nitric acid additions should be made with 42° Baume (~67%) nitric acid to avoid excessive reduction of specific gravity.

Stainless steel tanks, coils and heaters rely on the presence of nitric acid to prevent corrosive attack, so the nitric acid content should not be allowed to drop below 2%.

The addition of water to lower the specific gravity is only necessary if the specific gravity exceeds 1.80 (80°F/60°F)/27°C/16°C). Water addition should be made only when the appropriate amounts of virgin Phosbrite solution and nitric acid have been made and the specific gravity exceeds the recommended parameter.

Occasionally, when the water content of a Phosbrite bath drops too low, a condition called “icing” may occur. Unlike the DAB bath, the “ice” formed in a Phosbrite bath produces small needle-like markings on the surface of the part. This condition is usually accompanied by a decrease in the specific gravity as the aluminum sulfate precipitates from the solution. Should this problem arise, add water and increase bath temperature until the “ice” is dissolved. Then, bring the bath to its normal operating parameters before resuming production.

Contamination due to oils, greases, and buffing compounds which have been dragged into the Phosbrite bath will create a black scum on the surface of the solution. This should be skimmed off if it occurs. Contamination of this nature will increase the rate of attack and may lead to reduced brightening. Proper cleaning and rinsing will minimize this situation.

Removal of the copper salt smut is required prior to anodizing. A 35% by weight, nitric acid solution or any proprietary desmut which will remove copper salts is acceptable.

The analytical procedures for determining nitric acid concentration, aluminum content, and the specific gravity, which have been described previously are all applicable to the analysis of a Phosbrite solution. Tables 6 or 7 respectively can also be used to determine the amount of water and nitric acid to add to the bath to maintain proper operating conditions.

Safety and Handling

Phosbrite and DAB are a mixture of strong acids and are corrosive to skin, eyes, and mucous membranes. The fumes evolved during Bright Dipping are toxic and corrosive. The products do not burn but will emit toxic fumes when heated to high temperatures.

Rubber gloves, apron, and full face shield or chemical goggles must be used when handling these products. The Material Safety Data Bulletin for Phosbrite or DAB must be reviewed with all personnel who handle or come into contact with the products. A Material Safety Data Bulletin Sheet may be obtained at 847-849-4200 or from the PCS web site (www.nutrien.com).

Phosphoric Acid Storage System

In addition to the considerations mentioned earlier, phosphoric acid should be handled in a manner similar to that which is depicted in Figure 3. The tank foundation and dike should be built and sized in accordance with local requirements. Strong oxidizers and basic materials should not be contained in the same dike system as the phosphoric acid.

The storage tank and structurals should be constructed of 316L stainless steel, with one-inch fiberglass insulation and 10 Ga. 304 SS jacketing. The heating system should maintain the acid temperature above the freezing point, but below 120°F (between 77°F and 120°F).

The 316L piping should be insulated and jacketed. Drain points are recommended for the tank and all pipe sections for ease of maintenance.

During cleaning of the system, keep the temperature as low as possible. The lower temperature will minimize the high corrosion properties exhibited by weaker acid solutions at high temperatures.

For more information, please ask your PCS Sales Representative or Customer Service Representative for the *Purified Phosphoric Acid Technical Info Bulletin*.

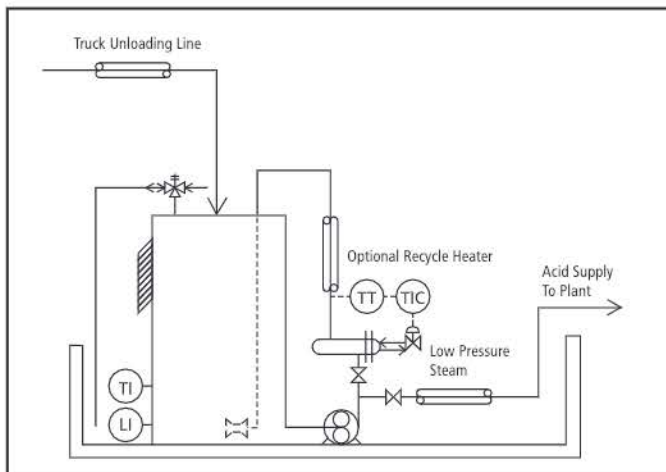


FIGURE 3: Schematic of Typical Phosphoric Acid Storage System

Aluminum Alloy

The brightness and smoothness of the finished part are also dependent on metallurgy of the aluminum itself. The metallurgical factors affecting brightness are: the amount of impurities (including alloying elements), the condition in which the impurities are present, and the crystalline grain structure of the aluminum (from either heat treatment or physical stretching or bending).

Magnesium is the only element that can be alloyed with aluminum to increase strength without drastically reducing brightening characteristics. Because magnesium is the metallic element with properties closest to aluminum, it is not surprising that magnesium interferes least with the brightening operation.

Iron is the most common impurity causing loss of brightness; therefore, control of this impurity is important in all bright work alloys. All so-called super-bright alloys have a limit of approximately 0.1% iron maximum (approx. 1000 ppm).

Silicon also reduces brightening characteristics and must be carefully controlled. Important exceptions to this are extrusion alloys such as 6063 and 6463 which contain 0.2 to 0.6% silicon for improved formability. The silicon, if bound in the form of magnesium silicide apparently does not interfere with brightening as much as large aggregates do when precipitated at the grain boundaries. This precipitation normally results from poor quenching after extrusion or heat treatment and by over-buffing. It can appear as white "mottling" or white blotches after Bright Dip rinses or after anodizing.

In addition to the presence of elements other than aluminum, the grain structure of the alloy is important. From a brightening viewpoint, the alloy should be as small grained as possible and in addition, all impurities (including alloying elements) should be homogeneously distributed. However, physical working properties of the alloy are as important as the finishing characteristics, and often additional treatments must be given to the alloy to give the desired forming characteristics regardless of the effect on brightness. For a given aluminum composition a slightly faster rate of attack will occur with hard temper metal as opposed to fully annealed or soft metal. In general, harder tempers produce the brightest work. Large grain size causes "orange peel" which becomes more pronounced as increasing amounts of metal are removed from the surface.

Procedure for Analyzing the Bright Dip Bath

The operating aluminum Bright Dip bath is composed of four major components — phosphoric acid, aluminum, nitric acid and water. Determination of three of these components allows calculation of the fourth, usually water, by difference. The specific gravity of the bath is also a function of the composition. Common practice is to use the specific gravity as a direct indicator of the water content (if the approximate aluminum content is known).

1. Sampling Procedure

Obtain approximately 200 ml of sample (in a 400 ml breaker) from the Bright Dip tank. Be sure the tank is thoroughly agitated and that the sample is withdrawn from under the surface (to avoid contamination by impurities floating on the surface). If additions have been recently made, allow enough time for thorough mixing (30-40 min.).

Cover the beaker and allow it to cool to room temperature (using a cooling bath if available), or the sample may be cooled in a graduated cylinder or hydrometer jar in preparation for the specific gravity determination. Allow to stand long enough so that all air bubbles have escaped from the sample (thirty minutes is usually sufficient).

2. Specific Gravity Determination

A specific gravity measurement should be made at least once and preferably twice a shift. Water additions can be calculated using the water addition chart (Table 6) on pages 20-21.

3. Nitric Acid Determination

A nitric acid analysis should be performed using the procedure on page 22. The sample for the nitric acid determination should be taken at the same temperature the specific gravity is measured.

4. Aluminum Determination

The aluminum concentration should be determined using the procedure on page 25. The aluminum concentration should be checked at least once each week.

Measurement of Specific Gravity

Applicability

This method is applicable to the determination of specific gravity or relative water content of phosphoric acid aluminum Bright Dipping baths.

Principle

For a given aluminum concentration, the amount of water in the Bright Dip solution is directly related to the specific gravity (weight) of the Bright Dip solution. The amount of water necessary to correct for boil out can be calculated using the specific gravity and Table 6 pp. 20-21.

Apparatus

- | | |
|---------------------------------------|--------------------------------|
| 1. Hydrometer (60°F/60°F)/(16°C/16°C) | Range, approximately 1.68–1.74 |
| 2. Graduated Cylinder | 100 ml or hydrometer jar |
| 3. Thermometer (non-Mercury) | 0 – 212°F, -18 – 100°C |
| 4. Constant Temperature Bath | Optional |

Procedure

1. Pour approximately 80 ml of the sample into a 100 ml graduate (or other suitable tube). Measure the temperature of the sample at 80°F/27°C.
2. Introduce the hydrometer into the graduated cylinder or hydrometer jar. Read the specific gravity value only after the hydrometer has come to equilibrium (approximately 5 minutes) and temperature of 80°F.

TABLE 6: Water Addition Chart (Specific Gravity Correction)

Specific Gravity Units	Bath Volume in Gallons						
	300	400	500	600	700	800	900
.001	0.4	0.6	0.7	0.8	1.0	1.0	1.3
.003	1.3	1.7	2.1	2.5	2.9	3.6	3.8
.005	2.1	2.8	3.5	4.2	4.9	5.6	6.3
.007	2.9	3.9	4.9	5.9	6.9	7.8	8.8
.009	3.8	5.0	6.3	7.6	8.8	10.0	11.3
.010	4.2	5.6	7.0	8.4	9.8	11.2	12.6
.011	4.6	6.2	7.7	9.2	10.8	12.4	13.8
.013	5.6	7.3	9.1	10.9	12.7	14.6	16.4
.015	6.5	8.4	10.5	12.6	14.7	16.8	19.4
.017	7.3	9.5	11.9	14.6	16.6	19.0	21.9
.019	8.2	10.6	13.3	16.3	18.6	21.2	24.5
.020	8.6	11.2	14.0	17.2	19.6	22.4	25.8
.021	9.0	11.8	14.7	18.1	20.6	23.6	27.1
.023	9.9	12.9	16.1	19.8	22.5	25.8	29.7
.025	10.5	14.0	17.5	21.0	24.5	28.0	31.5
.027	11.3	15.1	18.9	22.7	26.4	30.2	34.0
.029	12.2	16.2	20.3	24.3	28.4	32.4	36.5
.030	12.6	16.7	21.0	25.1	29.4	33.4	37.8
.031	13.0	17.4	21.7	26.0	30.3	34.8	39.0
.033	13.8	18.5	23.0	27.7	32.3	37.0	41.5
.035	14.7	19.6	24.5	29.4	34.3	39.2	41.4
.037	15.5	20.7	25.9	31.0	36.2	41.4	46.6
.039	16.4	21.8	27.3	32.7	38.1	43.4	49.1
.040	16.8	23.4	28.0	33.6	39.2	46.8	50.3
.045	18.9	25.2	31.5	37.8	44.1	50.4	56.6
GALLONS OF WATER YOU WOULD ADD							
Specific Gravity Units	Bath Volume in Gallons						
	1000	1200	1400	1500	1600	1800	2000
.001	1.4	1.7	2.0	2.1	2.2	2.5	2.8
.003	4.2	5.0	5.9	6.3	6.7	7.6	8.4
.005	7.0	8.4	9.8	10.4	11.2	12.6	14.0
.007	9.8	11.7	13.7	14.7	15.7	17.6	19.6
.009	12.6	15.1	17.6	18.9	20.1	22.6	25.2
.010	14.0	16.7	19.6	21.0	22.4	25.2	28.0
.011	15.4	18.5	21.5	23.1	24.6	27.7	30.8
.013	18.2	21.8	25.3	27.3	29.1	32.7	36.4
.015	21.0	25.2	29.4	31.5	33.6	38.7	42.0
.017	23.8	29.2	33.3	35.7	38.0	43.9	47.6
.019	26.6	32.7	37.2	39.9	42.5	49.0	51.3
.020	28.0	33.8	39.2	42.0	44.8	51.6	55.9
.021	29.4	36.1	41.1	44.1	47.0	54.2	58.7
.023	32.1	39.6	45.0	48.3	51.5	59.3	64.3
.025	35.0	42.0	49.0	52.4	56.0	62.9	69.9
.027	37.8	45.3	52.9	56.6	60.4	68.0	75.5
.029	40.6	48.7	56.8	60.8	64.9	73.0	81.1
.030	42.0	50.3	58.7	62.9	67.1	75.5	83.9
.031	43.1	52.0	60.7	65.0	69.4	78.0	86.7
.033	46.1	55.4	64.6	69.2	73.8	83.7	92.3
.035	49.0	58.7	68.5	73.4	78.3	88.1	97.9
.037	51.7	62.1	72.4	77.6	82.8	93.1	103.5
.039	54.5	65.5	76.4	81.8	87.3	98.2	109.1
.040	55.9	67.1	78.3	83.9	89.5	100.7	111.9
.045	62.9	75.7	88.1	94.4	100.7	113.3	125.9
GALLONS OF WATER YOU WOULD ADD							

To decrease the specific gravity by the amount in column one, determine the volume of Bright Dip solution on the top row and add the corresponding amount of water.

Water Addition Chart (cont.)

Specific Gravity Units	Bath Volume in Gallons						
	2100	2200	2400	2500	2600	2800	3000
.001	1.9	3.1	3.4	3.5	3.6	3.9	4.1
.003	8.8	9.2	10.1	10.5	10.9	11.7	12.6
.005	14.7	15.4	16.8	17.5	18.2	19.6	21.0
.007	20.6	21.5	23.5	24.5	25.5	27.4	29.4
.009	26.4	37.7	30.2	31.5	32.7	35.2	37.8
.010	29.3	30.8	33.6	35.0	36.4	39.2	42.0
.011	32.3	33.8	36.9	38.5	40.0	43.1	46.2
.013	38.2	40.0	43.6	45.5	47.3	50.9	54.5
.015	44.1	46.2	50.3	52.4	54.5	58.7	62.9
.017	49.9	52.3	58.5	59.4	61.8	66.6	71.3
.019	55.8	58.5	65.4	66.4	69.1	74.4	79.7
.020	58.7	61.5	67.6	69.9	72.7	78.3	83.9
.021	61.7	64.6	72.2	73.4	76.4	82.2	88.1
.023	67.6	79.8	79.1	80.4	83.6	90.1	96.5
.025	73.6	76.9	84.0	87.4	90.9	97.9	104.9
.027	79.3	83.1	90.6	94.4	98.8	105.7	113.3
.029	85.2	89.2	97.3	101.4	105.5	113.6	121.7
.030	88.1	92.3	100.7	104.9	109.1	117.5	125.9
.031	81.0	95.4	104.1	108.4	112.7	121.4	130.0
.033	96.9	101.5	110.8	115.4	120.0	129.2	138.5
.035	102.8	107.7	117.5	122.4	127.3	137.1	146.9
.037	108.7	113.8	124.2	129.4	134.5	144.9	155.2
.039	114.5	120.0	130.9	136.4	141.8	152.7	163.6
.040	117.5	123.1	134.3	139.7	145.5	156.6	167.8
.045	132.2	138.5	151.0	157.3	163.6	176.2	188.8
GALLONS OF WATER YOU WOULD ADD							
Specific Gravity Units	Bath Volume in Gallons						
	3200	3400	3500	3600	3800	4000	5000
.001	4.5	4.8	4.9	5.0	5.3	5.6	7.0
.003	13.5	14.3	14.7	15.1	15.9	16.8	21.0
.005	22.5	23.8	24.5	25.2	26.6	28.0	35.0
.007	31.5	33.9	32.3	35.2	37.2	39.2	49.0
.009	40.6	42.8	44.1	45.3	47.8	50.3	63.0
.010	45.1	47.5	49.0	50.3	53.1	55.9	69.9
.011	49.6	52.3	53.8	55.4	58.5	61.5	76.9
.013	58.6	61.8	63.6	65.5	69.1	72.7	90.9
.015	67.6	71.3	73.4	77.4	79.7	83.9	104.9
.017	76.6	80.8	83.2	87.7	90.3	95.1	118.9
.019	85.6	90.3	93.0	98.1	101.0	106.3	132.9
.020	90.1	95.1	97.9	103.2	106.3	111.9	139.9
.021	94.6	99.9	102.8	108.4	111.6	117.5	146.9
.023	103.7	109.4	112.6	118.7	122.2	128.7	160.8
.025	112.7	118.9	122.4	125.9	132.9	139.9	174.8
.027	121.7	128.4	132.2	135.9	143.5	151.0	188.8
.029	130.7	137.9	142.0	146.0	154.1	162.2	209.8
.030	135.7	142.7	146.9	151.0	159.4	167.8	209.8
.031	139.7	147.4	151.7	156.1	164.8	173.4	216.8
.033	148.7	156.9	161.5	166.2	175.4	184.6	230.8
.035	157.7	166.4	171.3	146.2	186.0	195.8	244.7
.037	166.8	175.9	181.1	186.3	196.6	207.0	258.7
.039	175.8	185.5	190.9	196.4	207.3	218.2	272.7
.040	180.3	190.2	195.8	201.4	212.6	223.8	279.7
.045	202.8	214.0	220.3	226.6	239.2	251.7	314.7
GALLONS OF WATER YOU WOULD ADD							

To decrease the specific gravity by the amount in column one, determine the volume of Bright Dip solution on the top row and add the corresponding amount of water.

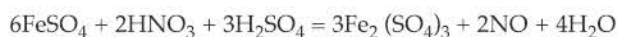
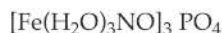
Determination of Nitric Acid (Ferrous Ammonium Sulfate Titration)

Applicability

This method is applicable to the determination of nitric acid in DAB and Phosbrite baths.

Principle

In the presence of sulfuric acid, ferrous ammonium sulfate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) reacts with nitric acid to form ferric sulfate and nitric oxide. At the endpoint of the titration, excess ferrous ammonium sulfate reacts with the dissolved nitric oxide to form an intense brown complex:



Reagents

- | | |
|-----------------------------------|---|
| 1. Phosphoric Acid | 85% Reagent Grade |
| 2. Ferrous Ammonium Sulfate (FAS) | with factor of approximately 0.70. Preparation and standardization described at end of procedure. |

Apparatus

- | | |
|---|--|
| 1. Pyrex Beaker | 150 ml |
| 2. Graduated Cylinder | 100 ml |
| 3. Hot Plate | Stirring hot plate and small stirring bar is preferred |
| 4. Titrating Burette | 10 ml |
| 5. Syringe ¹ | 2 ml |
| 6. Thermometer (non Hg) | 0–212°F, -18–100°C |
| 7. Hydrometer (60°F/60°F)/
(16°C/16°C) | 1.6–1.8 Range |

Procedure

1. Measure a 2.0 ml sample of Bright Dip solution by introducing the syringe tip just below the surface of the sample and withdrawing the plunger halfway. The syringe should then be inverted and the air bubble forced out of the tip. Then fill the syringe past the 2 ml mark and push the plunger carefully back to the 2 ml mark. The tip of the syringe should be touched to the side of the sample beaker to remove any droplets. The 2 ml sample should be forced into 150 ml beaker containing 50 ml of 85% phosphoric acid, touching the tip to the side of the beaker at the end of the delivery. Do not use a flask as the fumes evolved must be freely released from the solution.
2. Heat the beaker to 125°F/52°C and quickly titrate dropwise with the ferrous ammonium sulfate solution (FAS) stirring well until a permanent brownish color appears. Towards the end of the titration, the acid will "boil" or effervesce with each addition of ferrous ammonium sulfate, and the characteristic reddish-brown fumes of nitrogen dioxide will be given off. The final temperature must be between 130°F/54°C and 140°F/60°C.

Notes:

1. A syringe must be used due to the viscosity of the Bright Dip solution.

Calculation:

$$\begin{array}{l} \% \text{ HNO}_3 \\ \text{(by weight)} \end{array} = \frac{\text{ml} \times \text{factor}}{\text{Specific Gravity}}$$

Notes:

Preparation of Ferrous Ammonium Sulfate:

Dissolve 230 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, C.P. in 500 ml of distilled water containing 50 ml of concentrated H_2SO_4 in a 1000 ml volumetric flask. Dilute to the mark with distilled water.

Standardization of Ferrous Ammonium Sulfate (FAS) Solution

This solution should be standardized by titrating a 2 ml sample of solution (made by mixing 95 parts by volume of 85% reagent H_3PO_4 and 5 parts by volume of 70% reagent HNO_3) by the procedure as listed previously. The HNO_3 should be pipetted and both nitric acid and phosphoric acid should be at room temperature (about 80°F).

The factor is calculated as follows:

$$\text{Factor} = \frac{4.96}{\text{ml of Ferrous Ammonium Sulfate Solution Required}}$$

Factor on fresh solution should be about 0.7.

TABLE 7: Nitric Acid Addition Chart

% by weight HNO ₃	Bath Volume in Gallons														
	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	
.1	.5	.7	.9	1.0	1.2	1.4	1.5	1.7	1.9	2.1	2.2	2.4	2.6	2.7	
.2	1.3	1.4	1.7	2.1	2.4	2.7	3.1	3.4	3.8	4.1	4.4	4.8	5.1	5.5	
.3	1.5	2.1	2.6	3.1	3.6	4.1	4.6	5.1	5.6	6.2	6.7	7.2	7.7	8.2	
.4	2.1	2.7	3.4	4.1	4.8	5.5	6.2	6.8	7.5	8.2	8.9	9.6	10.3	10.9	
.5	2.6	3.4	4.3	5.1	5.6	6.9	7.7	8.6	9.4	10.3	11.1	11.9	12.8	13.7	
.6	3.1	4.1	5.1	6.2	7.2	8.2	9.2	10.3	11.3	12.3	13.3	14.4	15.4	16.4	
.7	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	
.8	4.1	5.5	8.8	8.2	9.6	10.9	12.3	13.7	15.1	16.4	17.8	19.2	20.5	21.9	
.9	4.6	6.3	7.7	9.2	10.8	12.3	13.9	15.4	16.8	18.5	20.0	21.5	23.1	24.6	
1.0	5.1	6.8	8.6	10.3	12.0	13.7	15.4	17.1	18.8	20.5	22.2	23.9	25.6	27.4	
1.1	5.7	7.5	9.4	11.3	13.2	15.1	17.0	18.8	20.7	22.6	24.4	26.3	28.2	30.1	
1.2	6.2	8.2	10.3	12.3	14.4	16.5	18.5	20.5	22.5	24.4	26.7	28.7	30.8	32.8	
1.3	6.7	8.9	11.1	13.4	15.6	17.7	20.0	22.2	24.4	26.7	28.9	31.1	33.3	35.6	
1.4	7.2	9.6	12.0	14.4	16.8	19.2	21.6	23.9	26.3	28.7	31.1	33.5	35.9	38.3	
1.5	7.7	10.3	12.8	15.4	18.0	20.6	23.1	25.7	28.2	30.8	33.3	35.9	38.5	41.0	
1.6	8.2	11.0	13.7	16.4	19.2	21.9	24.6	27.4	30.1	32.8	35.6	38.2	41.0	43.8	
1.7	8.7	11.6	14.5	17.5	20.4	23.3	26.2	29.1	32.0	34.9	37.8	40.6	43.6	46.5	
1.8	9.3	12.3	15.4	18.5	21.6	24.7	27.7	30.8	33.8	36.9	40.0	43.0	46.2	49.2	
1.9	9.8	13.0	16.3	19.5	22.8	26.0	29.3	32.5	35.7	39.0	42.2	45.4	48.7	52.0	
2.0	10.3	13.7	17.2	20.6	24.0	27.4	30.8	34.2	37.4	41.0	44.4	47.8	51.3	54.7	
GALLONS OF HNO ₃ YOU WOULD ADD															

% by weight HNO ₃	Bath Volume in Gallons														
	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000	
.1	2.9	3.1	3.2	3.4	3.6	3.8	3.9	4.1	4.3	4.4	4.6	4.8	5.0	5.1	
.2	5.8	6.2	6.4	7.2	7.2	7.5	7.9	8.2	8.6	8.9	9.2	9.6	9.9	10.3	
.3	8.7	9.2	9.7	10.3	10.8	11.3	11.8	12.3	12.8	13.3	13.9	14.4	14.9	15.4	
.4	11.6	12.3	13.0	13.7	14.4	15.0	15.7	16.4	17.1	17.8	18.5	19.2	19.8	20.5	
.5	14.5	15.4	16.2	17.1	18.0	18.8	19.7	20.5	21.4	22.2	23.1	23.9	24.8	25.7	
.6	17.4	18.5	19.5	20.5	21.5	22.6	23.6	24.6	25.7	26.7	27.7	28.7	29.8	30.8	
.7	20.3	21.6	22.7	23.9	25.1	26.3	27.5	28.8	29.9	31.1	32.3	33.6	34.7	35.9	
.8	23.3	24.6	26.0	27.4	28.7	30.1	31.5	32.8	34.2	35.6	36.9	38.3	39.7	41.0	
.9	26.2	27.7	29.2	30.8	32.3	33.9	35.4	36.9	38.5	40.0	41.6	43.1	44.6	46.2	
1.0	29.1	30.8	32.5	34.2	35.9	37.6	39.3	41.0	42.8	44.5	46.2	47.9	49.6	51.3	
1.1	32.0	33.9	35.7	37.6	39.5	41.1	43.3	45.1	47.0	48.9	50.8	52.7	54.5	56.4	
1.2	34.9	36.9	39.0	41.0	43.1	45.1	47.2	49.2	51.3	53.4	55.4	57.5	59.5	61.6	
1.3	37.8	40.0	42.2	44.5	46.7	48.9	51.1	53.4	55.6	57.8	60.0	62.2	64.5	66.7	
1.4	40.7	43.1	45.5	47.9	50.3	52.7	55.1	57.5	59.9	62.2	64.6	67.0	69.4	71.8	
1.5	43.6	46.2	48.7	51.3	53.9	56.4	59.0	61.6	64.1	66.7	69.6	71.8	74.4	77.0	
1.6	46.5	49.2	52.0	54.7	57.5	60.2	62.9	65.7	68.4	71.1	73.9	76.6	79.3	82.1	
1.7	49.4	52.3	55.2	58.1	61.0	64.0	66.9	69.8	81.7	75.6	78.5	81.4	84.3	87.2	
1.8	52.3	55.4	58.5	61.6	64.6	67.7	70.8	73.9	77.0	80.0	83.1	86.2	89.3	92.3	
1.9	55.2	58.5	61.7	65.0	68.1	71.5	74.7	78.0	81.2	84.5	87.7	91.0	94.2	97.5	
2.0	58.1	61.6	65.0	68.4	71.8	75.2	78.7	82.1	85.5	88.9	92.3	95.8	99.2	102.6	
GALLONS OF HNO ₃ YOU WOULD ADD															

0.6% by wt. = 1% by vol.

3% by wt. = 5% by vol.

To increase the nitric acid concentration by the percent in column one, determine the volume of Bright Dip solution on the top row and add the corresponding amount of 70% nitric acid.

Determination of Aluminum Concentration (EDTA Method)

Applicability

This method is applicable to the determination of aluminum in DAB and Phosbrite baths. An appreciable amount of any polyvalent cation other than dissolved aluminum will interfere in this titration.

Principle

This method used EDTA which is a chelating agent that reacts slowly with aluminum. In this titration excess EDTA is added to the Bright Dip solution and allowed to react with the aluminum for at least 10 minutes to ensure complete reaction. Copper, which reacts quickly with EDTA, is used for the back titration to determine the excess EDTA, using pyrocatechol-violet as the indicator. Free copper, present only at the end of titration, turns this indicator from pale yellow-green to bright blue.

Reagents

- | | |
|------------------------------------|--|
| 1. Dilute Ammonium Hydroxide | Dilute reagent grade ammonium hydroxide 1 to 4 with distilled water. |
| 2. Pyridine Solution | 10% Solution, Dilute 100 ml reagent grade pyridine with 900 ml distilled water. The final pH should be 6.0–7.0. |
| 3. Indicator Solution | Dissolve 0.1 grams reagent grade pyrocatechol violet in 100 ml distilled water. |
| 4. EDTA Stock Solution | 0.1 M, Dissolve 37.21 grams of reagent grade disodium ethylene-diamine tetraacetate dihydrate (EDTA) in distilled water in a one liter volumetric flask and dilute to the mark with distilled water. |
| 5. EDTA Working Solution | 0.01 M, Dilute 100 ml of the EDTA Stock Solution to the mark in a 1 liter volumetric flask with distilled water. |
| 6. Copper Sulfate | 0.1 M, Dissolve 24.97 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Stock Solution in distilled water and dilute to the mark in a 1 liter volumetric flask. |
| 7. Copper Sulfate Working Solution | 0.01 M, Dilute 100 ml of the Copper Sulfate Stock Solution to the mark with distilled water in a 1 liter volumetric flask (Note 1). |

Apparatus

- | | |
|----------------------------------|-------------------------|
| 1. Volumetric Flasks | 1 liter, 250 ml, 100 ml |
| 2. Erlenmeyer Flask | 250 ml |
| 3. Titrating Burette | 50 ml |
| 4. Syringe ¹ | 1.0 ml |
| 5. Pipets | 10 ml, 15 ml |
| 6. pH Meter or pH Paper | Range pH 6–7 |
| 7. Hydrometer (Specific Gravity) | Range 1.6–1.8 |

Notes:

1. A syringe must be used due to the viscosity of the Bright Dip solution.

Procedure

1. Introduce 0.5 ml of the sample (using the 1.0 ml syringe) into a 100 ml volumetric flask and dilute to the mark with distilled water — mix well. (Note 2)
2. Pipet 10 ml of the diluted solution (Step 1) and 15 ml of the 0.01 M EDTA Solution into a 250 ml Erlenmeyer flask. Allow a waiting period of at least 10 minutes but, not more than 1 hour.
3. Add 100 ml of distilled water and adjust the pH to between 6.0 and 6.2 with the diluted ammonium hydroxide (using pH meter). This should take 5 to 8 drops. (Note 3)
4. Add 10 ml pyridine and 6 to 10 drops of the indicator solution and titrate rapidly with the 0.01 M Copper Sulfate Solution. Record the number of ml required to reach the end point. (Note 4)

Calculations:

$$\frac{(15 - \text{ml copper sulfate solution}) \times 2.44}{\text{specific gravity}} = \% \text{ AlPO}_4$$

$$\frac{(15 - \text{ml copper sulfate solution}) \times 0.54}{\text{specific gravity}} = \% \text{ Al}$$

$$(15 - \text{ml copper sulfate solution}) \times 5.40 = \text{g/L of Al}$$

Notes:

1. The 0.01 M copper sulfate solution should be standardized against the 0.01 M EDTA solution by running a blank through the procedure, eliminating the 10 ml of sample solution and the subsequent neutralization with the dilute ammonium hydroxide. Exactly 15.0 ml of the copper sulfate solution should be required to reach the end point. If more or less is required, fresh solution exactly 0.01 M should be obtained from PCS Sales Technical Service Department. See contact list on page 44.
2. The specific gravity of the Bright Dip solution at the temperature at which the sample is taken should also be obtained so that the aluminum may be calculated by weight.
3. If the pH of the solution is adjusted over 6.8, the sample must be discarded and a fresh sample taken.
4. The end point is a color change from yellow-green to bright blue. Speed is essential as the end point will fade back to the yellow-green upon standing. The titration should be performed several times with the "blank" until the operator becomes familiar with the method.

References

1. *Chemist Analyst*, Vol. 45, No. 2, Page 35, June 1956.

RINSING

Though rinsing is not usually considered to be a finishing process, proper rinsing is essential to the production of high quality bright anodized aluminum. Proper rinsing is required to stop the reaction of the Bright Dip on the aluminum parts, reduce contamination of the processing tanks and leave the parts clean for subsequent finishing steps. Chemicals used in one finishing step are contaminants that interfere in subsequent process steps. For example, cleaners carried into the Bright Dip can cause pitting, dull parts and transfer etch because cleaners reduce the surface tension of the Bright Dip, and therefore, interfere in the chemical brightening process. Bright Dip solution (phosphoric acid) carried over to the anodize tank will cause a soft anodic coating to form. Phosphate in the seal tank will interfere with sealing and cause smutting, and high levels prohibit sealing altogether.

Thorough rinsing is achieved by optimizing the following:

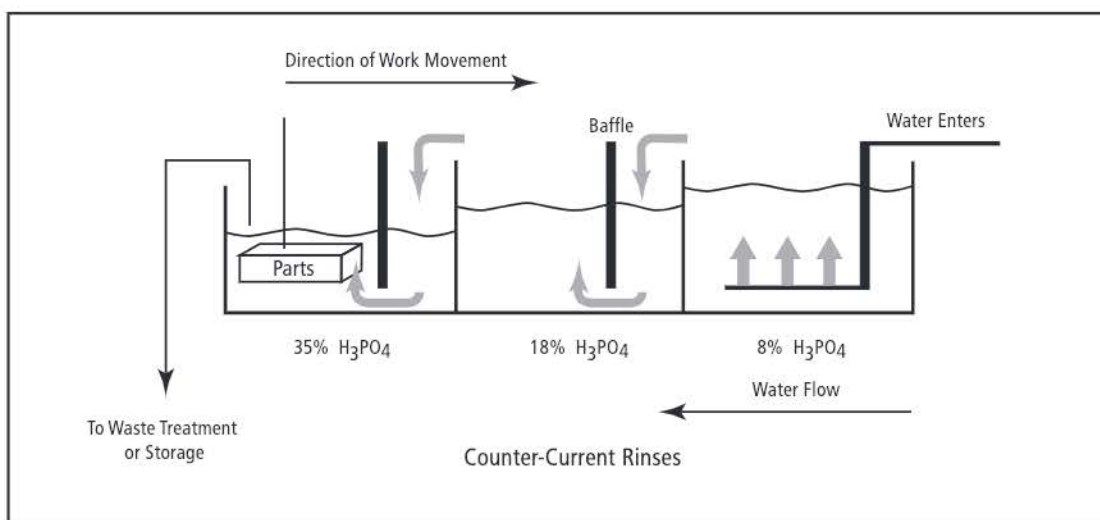
1. Number and configuration of rinses
2. Type of rinse
3. Drain time
4. Rack design
5. Size and shape of parts
6. Contaminants being rinsed

Each of these factors must be considered to optimize rinsing.

Number and Configuration of Rinses

The first consideration is the number of rinse tanks available. The more rinse tanks that are available, the lower the total water flow required to achieve proper rinsing. Whenever more than one rinse tank is available, counter-current rinsing should be used. The basic concept of counter-current rinsing is to use the water from previous rinsings to contact the more contaminated work. Fresh water enters the process at the final rinse stage and then moves in the opposite direction of the work flow to serve as rinse water for preceding rinse tanks as shown in Figure 4.

FIGURE 4: Counter-Current Rinsing



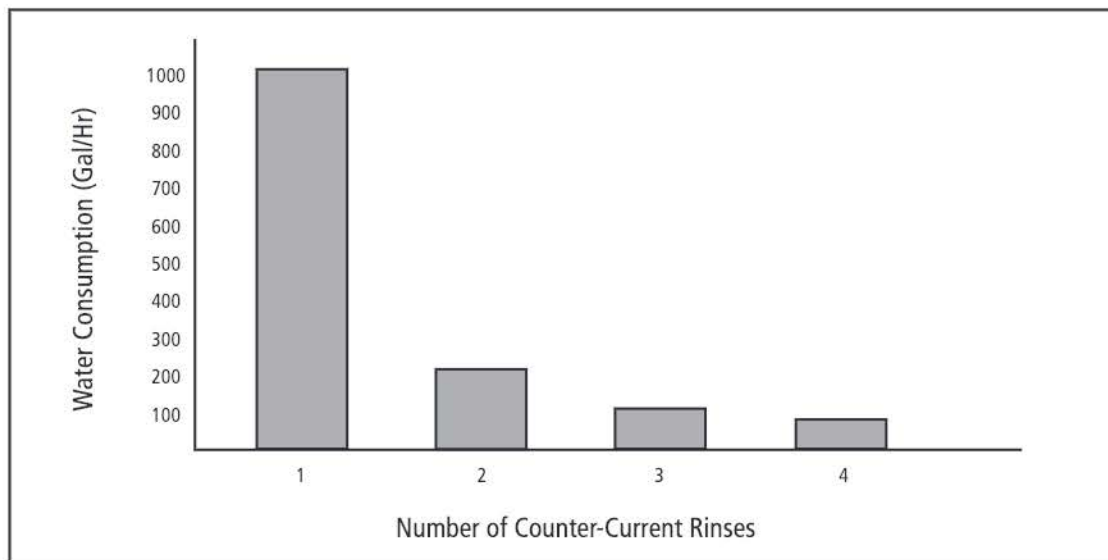
The amount of water required to properly rinse parts is greatly reduced when counter-current rinses are used. For example, if a flow rate of 1,000 gallons/hour is required to rinse parts properly using one rinse tank, 80–120 gallons/hour would be required for proper rinsing using a two-stage counter-flow rinse system, and only 8–12 gallons/hour would be required for a three-stage counter-flow system as shown in Figure 5.

As sewage and water treatment costs increase, the need for reduction in water usage becomes more important. Increasing the number of rinses and counter-flowing those rinses is an easy way to reduce water usage.

Another factor to consider when installing a multistage system is the need for agitation. In cases where water is cascading over a work piece, the high flow may provide adequate agitation. As more rinse stages are added to reduce the amount of water used, a point will be reached where the flow of water itself is not sufficient to provide adequate agitation. At this point air agitation will be required. This breaks up the interfacial resistance between the rinse water and the work surfaces and can penetrate recesses or hard to reach areas.

Whenever possible, drip pans should be installed between the tank lips. The pans should slant back toward the tank from which the rack is exiting to return some of the drag-out to that tank.

FIGURE 5: Water Savings with Counter-Current Rinsing

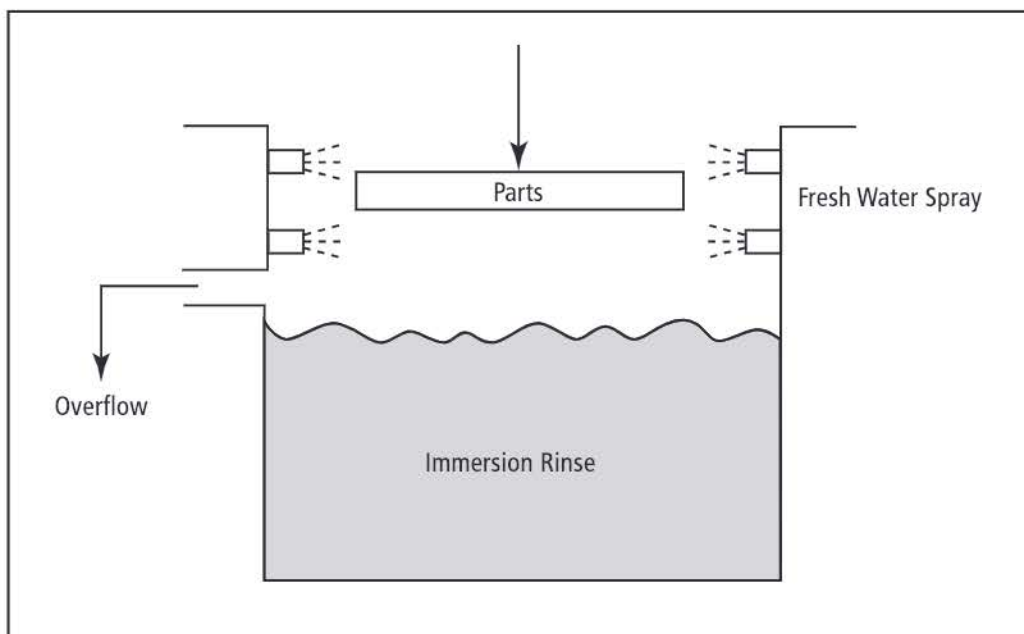


Type of Rinses

In addition to immersion rinsing, two types of spray rinses are used in the bright anodizing process. The most common form is an immersion and spray technique (see Figure 5). In this type of rinse the parts are immersed in an immersion rinse tank to remove the bulk of the contaminants. Then, as the parts exit the rinse tank, they are sprayed with clean water. The impact spray rinse is advantageous in removing stubborn films and permits lower water flows to the main immersion rinse because the last water contacting the part is clean and uncontaminated. This type of rinse is used primarily as a final rinse.

Impact spraying can also be used alone to remove contaminant films by both impact and diffusion. It uses less water than immersion rinsing, but it only rinses exposed surfaces. Spray rinsing cannot be used to rinse nested parts, tubing or other parts with inaccessible areas.

FIGURE 6: Spray and Immersion Rinse Combination



Drain Time

Drain time over processing tanks should be as long as possible, without causing solution to dry or leave permanent marks on the parts. This will keep drag-out to a minimum.

Rack Design, Size, and Shape of Parts

Racks should be designed to drain easily. Cup shaped parts on racks which can hold solution should be avoided whenever possible. Drag-out is also affected by the shape and position of the work. Racks should be designed to hold parts for maximum drainage. In some cases, holes have been drilled in parts to help drainage of cupped areas.

Occasionally, parts or racks are encountered that have crevices or folded areas. These recesses open in hot process tanks, like Bright Dip or cleaner tanks, but close up when they go into a cold rinse. This traps the process solution, and makes rinsing in a cold rinse impossible. Parts on racks with crevices or folds may require warm rinses to avoid contamination of processing tanks further down the line.

Recovery of Phosphoric Acid

One of the most effective cost-reduction measures available to the aluminum finisher is the recovery of phosphoric acid rinse water from the Bright Dipping operation. In addition to reducing phosphate discharge by up to 95 percent, a system can be designed to provide improved rinsing while recovering a valuable commodity for sale or reuse on the finishing line.

The actual savings realized via rinse water recovery can vary greatly, depending upon the design of the system and the operating practices of the finisher. A brief review of some of these considerations should be beneficial to the individual installing a new system, as well as the finisher seeking to upgrade an existing one.

Construction of Rinse Water Recovery System

The counter-current system shown in Figure 4 on page 27 includes a series of recovery rinses that can be counterflowed, followed by a free-flowing rinse. A pump can be included for transferring the recovered rinse water to a storage tank. Proper design provides for the correct number of tanks, adequate rinsing, and a recovered phosphoric acid of consistent quality.

The number of tanks added to an existing finishing line ultimately will be a compromise between recovery efficiency and available space. Because cost reduction is directly proportional to the volume of acid recovered, close attention should be paid to the ratio of recovered phosphoric acid versus that used in the Bright Dip. A rinse system with one stagnant tank can recover only 45 to 50 percent of the acid that is used. A two-tank system can recapture 60 to 65 percent, a three-tank system 80 to 85 percent, and a four-tank setup can recover 90 to 95 percent of the phosphoric acid used. The addition of a spray rinse on the final rinse tank can increase recovery efficiency 3 to 7 percent.

In each case, the series of recovery tanks must be followed by a free-flowing rinse to remove all remaining phosphates before anodizing. The three- and four-tank systems provide a higher recovery efficiency, and also reduced water consumption and less phosphate drag-out from the final rinse tank. All phosphoric acid not recovered must be neutralized or precipitated and removed by the waste-treatment system. Therefore, more efficient recovery systems permit the construction of smaller waste-treatment facilities and the reduction of associated chemical costs.

Design Pointers

Overlooking any of a number of elementary design factors may drastically reduce the overall efficiency of the finishing line. The following are some important considerations:

Water Flow

The counterflow system must be designed to prevent “short circuiting” during solution transfers. As solution is removed from the bottom of one end of each tank, rinse water from the following tanks should counter-flow into the top of the opposite end.

Solution Depth

Each successive rinse tank should cover 1 to 2 inches more of the splines than the previous rinse to ensure complete removal of the more concentrated solution. The final, flowing rinse should also allow the work bar to be completely immersed. This helps prevent phosphate contamination of seal tanks by reducing dried-on Bright Dip solution that would be washed in the seal tanks by steam condensation on the work bar.

Spray Rinsing

Though called a free flowing rinse, the final rinse tank may have all its makeup water supplied by high-pressure spray rinsing of each rack as it emerges from the tank as shown in Figure 6.

Agitation

Good agitation is essential for complete removal of the viscous film of Bright Dip solution from the parts. Each rinse tank must have two air lines running the length of the tank to supply high-volume, low-pressure, oil-free air. On a manually operated hoist line, the first recovery rinse should be large enough for the operator to rock or swing the work bar.

Drip Pans

Drip pans should be installed between all tanks so the solution drainage during transfer is returned to the most concentrated tank.

Freeboard

Adequate freeboard height must be provided to prevent solution from being splashed over the sides during rinsing. Six to eight inches is sufficient for most lines.

Operating Pointers

Even a well-designed recovery system can achieve a lower-than-expected recovery ratio due to poor control. A well-operated system will prevent fluctuations in the efficiency of rinsing and in the concentration of recovery acid. The following operating parameters will increase the amount of phosphoric acid recovered:

Pumping

The most efficient recovery systems have automated controls to pump a portion of the first recovery rinse to storage when the specific gravity reaches 1.30 (about 36 percent phosphoric acid). Because the Bright Dip solution is more readily miscible in a weak acid concentration than in water, no more than 20 percent of the tank should be replaced at any one time.

Concentration Control

If 20 percent of the first recovery rinse is replaced at one time, the acid concentration in that rinse will vary from 33 to 36 percent. Optimum recovery operation is achieved when the concentration variations are in this range. Recovery of acid at 38 percent or higher should be avoided due to the marked reduction in recovery efficiency at this concentration.

Temperature Control

The temperature in the first recovery rinse may be critical to the appearance of the parts. High temperatures can cause etching, mottling or pitting, while low temperatures result in poor rinsing. The temperature must be low enough to cool the parts rapidly and halt the action of the Bright Dip solution, but high enough to rapidly dilute the film of acid solution clinging to the part.

Heat transferred to the first rinse by the parts will rapidly raise the rinse temperature to the point that problems will occur. Cooling must therefore be provided. The cooling system must be able to hold the rinse temperature at 80°F/27°C for extrusions and at 90 to 100°F/32 to 37°C for stampings. It should be designed to prevent fluctuations of more than two degrees above or below the desired operating temperatures because a change of four or five degrees can drastically change the performance of the rinse.

Additional Information

The cost of phosphoric acid represents approximately 90 percent of the total chemical costs for bright anodizing lines. Even a small improvement in recovery efficiency can significantly reduce direct processing expenditures. In addition, any phosphoric acid not recovered must be neutralized before it can be discharged to a sewage system. This neutralization represents a substantial cost. Approximately one pound of 50% sodium hydroxide is required per pound of 80% phosphoric acid discharged.

PCS Sales Technical Service representatives are highly experienced in improving recovery efficiency.

ANODIZING

Anodizing is an electrochemical process for thickening the natural oxide coating always found on aluminum. This natural oxide coating is only 0.0005 mils thick, but the anodizing process can increase this film thickness to between 0.08 and 2.0 mils. This thicker oxide coating is more resistant to corrosion and abrasion than either the underlying aluminum or the aluminum with only its natural oxide coating. In addition, most anodized coatings are porous and have the ability to absorb dyes and pigments before they are sealed. This produces an attractive colored oxide coating, integral to the metal itself, and thus less likely to chip or peel than painted coatings. With proper care and handling anodized aluminum articles can last a lifetime.

Mechanism of Coating Formation

The formation of the aluminum oxide coating on aluminum involves two competing processes which occur simultaneously. Briefly, the aluminum parts are made the positive pole, or anode, in an electrochemical cell using an acidic electrolyte. As current passes through the solution, oxygen is generated at the anode and immediately reacts with the aluminum parts to form the aluminum oxide coating. Simultaneously, the aluminum oxide coating, which is soluble in the electrolyte, is dissolved by the acid and will become porous and less dense. (See Figure 7.)

FIGURE 7: Mechanism of Anodic Coating Formation

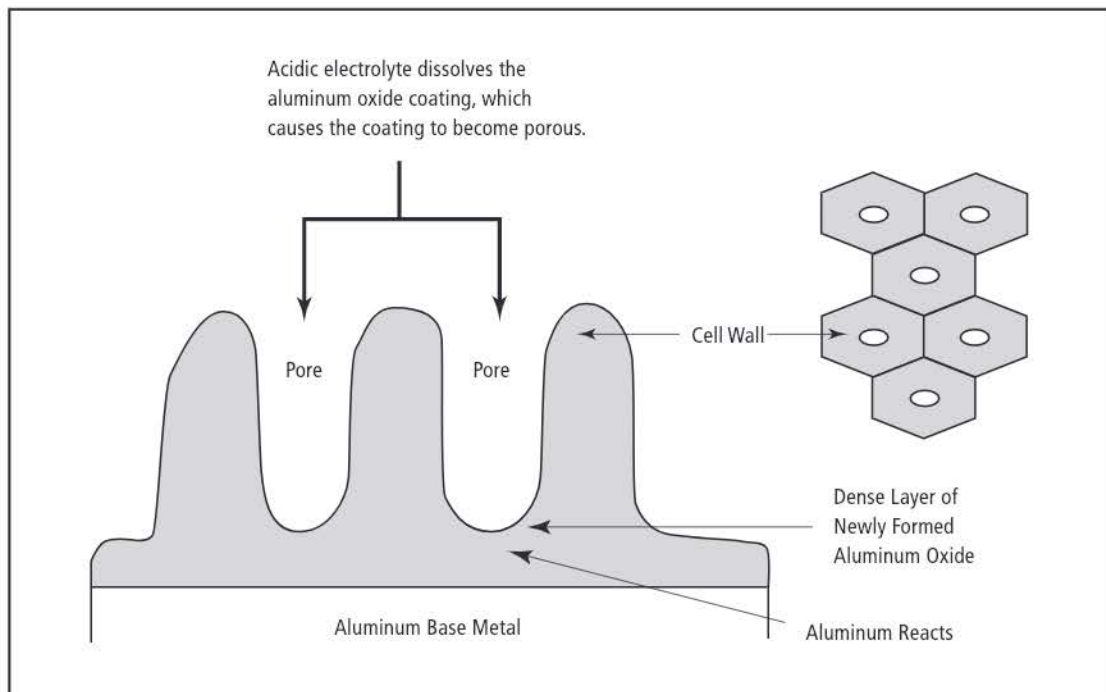


TABLE 8: Parameters Affecting Anodizing

Parameter	Recommended Operating Range	Increased Level	Decreased Level
ACID CONCENTRATION	Clear: 15% (by wt.) Dye: 18% (by wt.)	The higher the acid concentration the faster the anodic coating is dissolved and the more porous the coating. Darker dye color results, but more difficult to seal.	Lower acid concentration bath's conductivity and the porosity of the coating. Higher voltages required for anodizing.
TEMPERATURE	Clear: 68–72°F controlled +2°F Dye: 68–88°F controlled +1°F	As the temperature increases the rate of anodic coating dissolution increases. Coating, therefore, becomes very porous. A +2°F change in temperature will cause a significant change in porosity. For dye work control +1°F or color change will be apparent.	Decreasing the temperature decreases the porosity of the coating. The lack of porosity decreases the conductivity of the coating and oxygen diffusion rate. Higher voltage will be required to continue coating formation.
CURRENT	Clear: 8–12 amps/ft ² Dye: 10–15 amps/ft ²	Current density (not voltage) controls the rate of coating formation. Increasing the current density above 18–25 amps/ft can cause burns.	Decreasing the current density decreases the rate of coating formation, and may cause high porosity because the coating dissolves as it forms.
DISSOLVED ALUMINUM	2-12 gm/l	Above 12 gm/l Al the coating is noticeably cloudy.	Below 2 gm/l Al burning occurs at the contact because aluminum has a buffering effect in the bath and distributes current more evenly.
VOLTAGE	Clear: 12–18 volts Dye: 10–22 volts	Controls barrier layer cell size and wall thickness. Increased voltage is due to poor contact or racks.	Voltage is usually self regulating. It increases as the anodic coating builds on the part and its resistance increases.
TIME	Clear: 10–30 min. Dye: 10–60 min.	Coating thickness increases with time until the point where the coating dissolves at the same rate at which it forms (usually after 75 min.).	Decreasing time decreases the anodic coating thickness.
AIR AGITATION	Required for all Anodizing	Air agitation mixes the anodizing solution to allow uniform conditions in all parts of the tank. Heat generated at the parts by the anodizing process is removed. Agitation is necessary for uniform anodizing.	Decreased or insufficient agitation can cause streaks due to overheating, streaks due to accumulation of gases generated by anodizing and non-uniform anodic coating due to solution variation.

Control of Anodizing Baths

As the anodize bath is operated, solution is lost by drag-out on the parts and must be replaced by additions of sulfuric acid and water to maintain the proper solution level and strength in the anodize bath. In addition, aluminum oxide which is dissolved from the coating during anodizing causes aluminum to build up in the anodize bath. Proper monitoring of the chemical composition of the anodize bath is necessary to produce anodic coatings of good and uniform quality. As least once per shift the “free” sulfuric acid, specific gravity, and aluminum should be determined. Procedures for determining “free” sulfuric acid and aluminum are included at the end of this section.

In addition, agitation, dwell time, current density and temperature must be regulated to ensure an adherent, clear, protective coating.

Sufficient agitation is required to disperse the heat generated during the anodizing process. For the best quality work, there must be sufficient agitation to prevent the temperature at the part surface from rising more than 1.0°F (0.5°C) above the temperature of the anodize bath. Localized temperature variations will cause differences in porosity which become apparent if the part is subsequently dyed. Cooling or refrigeration is required to control the temperature of the anodize bath within the $\pm 2^\circ\text{F}$ ($\pm 1^\circ\text{F}$ for dye work) required for consistent anodizing.

Anodizing Problems

Rainbow

Variations in coating thickness along the length of a part produce color variations known as “rainbow.” This may be caused by loose or insufficient number of contacts, or by applying the current too rapidly. “Rainbow” may also be caused by improper cathode placement, causing thicker coatings near high cathode density areas.

Grayness

Grayness may occur when aluminum content in the anodize bath is too high or may be due to impurities in the alloy. In general, coatings with higher density tend to be darker or more cloudy.

Dullness

Alloying elements intentionally added to the aluminum for strength and forming characteristics can have a great effect on the color and clarity of the anodic coating. Alloys high in iron and silicon, even within the designated specification ranges, may produce noticeably dull coatings. In addition, high aluminum in the anodize solution will cause dull coatings. Alloying elements have the following effects on the coating color and clarity.

Iron:	Reduces brightness, hardness, and corrosion resistance.
Silicon:	Causes cloudy, gray appearance.
Magnesium:	The only alloying element that does not detract from the color or clarity of the anodic coat.
Manganese:	Reduces brightness and corrosion resistance. Causes yellow tint in anodic coat.
Magnesium Silicide (Mg_2Si):	Causes cloudy appearance known as mottling.
Copper:	Reduces brightness and corrosion resistance. Causes red tint in anodic coat.

Contamination

Phosphate contamination above 1,000 ppm will produce soft coatings that are difficult to seal.

Chloride and/or fluoride contamination may cause pitting above 50 ppm.

Soft Coatings

Soft coatings result when the anodic coating is applied too rapidly, when the temperature or acid concentration are too high, when the part is anodized too long (over 1 hr.) and when phosphate contamination is over 1,000 ppm.

Burns

Burns result from poor contacts or too few contacts, insufficient aluminum (below 2 gm/l) to buffer the current, large surges of power and poor agitation (causing extensive localized overheating). Brown burns near the end of the part may result from low acid concentrations.

Thin Coatings

Thin coatings may result from poor contacts, short time, low current density or high phosphate. Parts having thin coatings will typically be very bright and have a rainbowed appearance.

Determination of "Free" Sulfuric Acid in Aluminum Anodizing Baths

Reagents

1. 1.0 N Sodium Hydroxide (Standardized)
2. Methyl orange indicator solution

Apparatus

- | | |
|--|-----------|
| 1. Pipet | 10 ml |
| 2. Erlenmeyer Flask | 250 ml |
| 3. Titrating Burette (Teflon Stopcock) | 50 ml |
| 4. Hydrometer (Specific Gravity) Range | 1.0-1.225 |
| 5. Graduated Cylinder | 100 ml |

Procedure

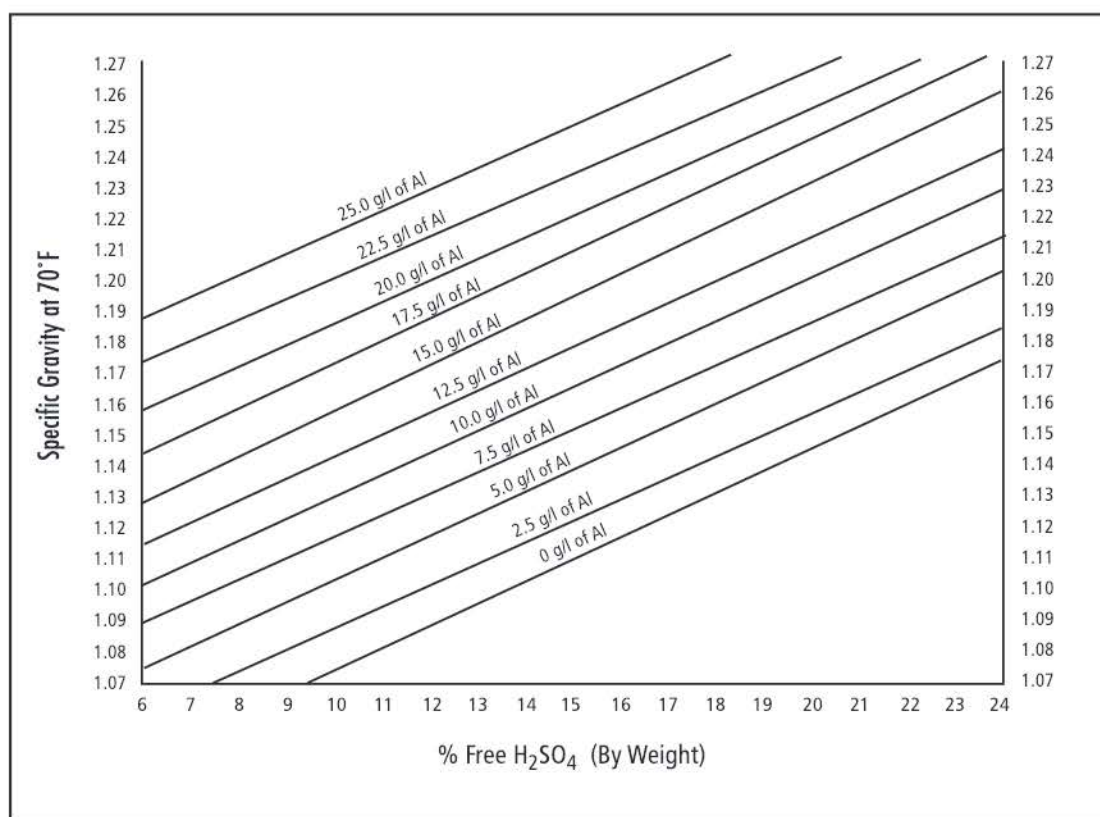
1. Pour sample into the 100 ml graduate and measure the specific gravity with the hydrometer, adjusting the temperature to 70°F ±2°F.
2. Introduce 10 ml of the anodizing solution (using a 10 ml pipet) into a 250 ml Erlenmeyer flask.
3. Add 50 ml of distilled water and 4 drops of methyl orange indicator.
4. Titrate with 1.0 N Sodium Hydroxide from a red to a yellow-orange color. (pH = 2.3)

Calculations:

1.
$$\frac{\text{ml of Sodium Hydroxide} \times N \times 0.49}{\text{Specific Gravity at } 70^{\circ}\text{F}} = \% \text{ "Free" Sulfuric Acid}$$

$$\text{ml of Sodium Hydroxide} \times N \times 4.9 = \text{grams/liter "Free" Sulfuric Acid}$$
2. Aluminum in grams/liter may be obtained from the graph (Figure 8). Aluminum may also be determined by the EDTA titration method (pp. 23–24). The sample size in step 1 is increased to 1.0 ml and the calculation is:
$$(\text{15 ml} - \text{ml of copper sulfate solution}) \times 2.7 = \text{g/L Al}$$

FIGURE 8: Relationship Between Specific Gravity, Free Sulfuric Acid and Aluminum Content of Anodizing Baths



SEALING

The anodic film produced on aluminum by sulfuric acid anodizing is very porous. This is due to the nature of the sulfuric acid electrolyte and its solvent action on the aluminum oxide film. This porous film must be “sealed” to fully protect the aluminum from corrosion. Although the coating is hard and abrasion-resistant, moisture and corrosive elements can penetrate to the underlying aluminum unless the pores are sealed. The resulting corrosion is unattractive and can cause weakening of the metal.

The purpose of sealing is to increase the corrosion resistance of the anodic coating. The most widely accepted theory of the mechanism of sealing is that a portion of the anodic film (aluminum oxide) is converted to an aluminum hydrate by immersion in hot water. Also occurring during sealing is the removal of acidic contaminants and the partial plugging of the pore openings of the coating with a hydrated aluminum oxide gel.

There are several types of seal baths, all composed of hot water with or without sealing additives. Nickel acetate and potassium dichromate have been popular as sealing additives. Nickel acetate has also proven very effective in what is known as the pre-seal, which came into use in the early 1970s and has become the standard in the industry for producing high quality seals.

Nickel Acetate Pre-Seal

As its name implies, the pre-seal is a preliminary sealing step and does not actually seal, or hydrate, the coating. It must be followed by a conventional seal such as hot water, nickel acetate or dichromate seal. The pre-seal prepares the anodic film for sealing by incorporating nickel ions in the film, thus partially plugging the pores. While the nickel is being incorporated in the film, the pre-seal is also removing sulfuric acid and aluminum sulfate from the film, thus preparing it to be hydrated in the final seal. The final seal is able to more completely and rapidly seal the anodic film and provide much greater corrosion resistance.

The pre-seal does not seal the anodic film because its operating temperature is too low for hydration to occur. Hydration of the coating will only occur in a seal bath having a temperature above 176°F/80°C; the most effective hydration occurs in the range of 203–212°F/95–100°C. There are no catalytic systems or other special bath additives known which can reduce the temperature requirements for rapid hydration of the coating.

The nickel acetate pre-seal should not be confused with the conventional nickel acetate seal. The pre-seal is operated at a high pH (6.8–7.2) and a low temperature (145–165°F)/(60–74°C), while the conventional nickel acetate seal is operated at a lower pH and a temperature close to boiling. The pre-seal also employs a dispersing agent not normally used in the conventional nickel acetate seal.

Contrary to popular belief, the nickel acetate pre-seal does not function better if the nickel is precipitated as the hydroxide. Early in its history, it was believed that the nickel must be present as nickel hydroxide. Current evidence indicates that only the nickel in solution is effectively incorporated in the anodic film.

Operating Conditions for the Nickel Acetate Pre-Seal

Proper pre-seal operation is required to provide adequate corrosion resistance for the anodic film, and also to maximize the pre-seal's operating life. Successful operation requires close attention to proper rinsing, proper control of operating conditions, and proper bath preparation. The following table indicates optimum conditions as well as normal operating ranges for the pre-seal.

TABLE 9: Recommended Operating Parameters for the Nickel Acetate Pre-Seal

	Range	Recommended
Nickel Acetate	1.5–4.0 grams/liter	2.0 grams/liter
Dispersant	1.5–4.0 grams/liter	2.5 grams/liter
pH	6.8–7.2	6.8–7.0
Temperature	140–165°F/60–74°C	160°F/74°C
Time	10–120 seconds	40 seconds

The dispersant should be of the condensed naphthylmethane sulfonate type, with a very low sulfate content. Lignin sulfonate dispersants have given erratic results in the past and should be avoided. There are currently a number of acceptable dispersants available which claim to be identical, but which have vastly different performance characteristics. It is extremely important to thoroughly investigate available dispersants and select the one which provides optimum performance in a given system.

The pH of the pre-seal should be checked every two hours and adjusted with acetic acid or 10% (by volume) ammonium hydroxide. The pH must never be adjusted higher than 7.2. If the parts are rinsed well, the pH should rise slowly during operation owing to volatilization of acetic acid. Frequent additions of ammonia to raise the pH are an indication of poor rinsing prior to the pre-seal. This causes increased smut formation and reduces the bath life.

Agitation must be provided to maintain uniformity and to prevent smut. The air should be supplied via two parallel air lines. The air must be oil-free blown, not compressed, air. Use of compressed air contaminates the tank with compressor oil and can cause a smut-like film on the parts.

The pre-seal bath must be carefully prepared. During the years that the pre-seal has been in use, the method for preparing the bath has evolved into one which has given excellent sealing with minimum smut formation.

Preparation of Nickel Acetate Pre-Seal

1. Thoroughly clean and rinse the tank, then fill with deionized water.
2. Preheat the tank to 110°F–120°F/43–49°C.
3. Adjust pH to 3.5–4.0 with acetic acid.
4. Predissolve the dispersant (2 g/L) in deionized water, making sure all the dispersant is in solution before adding to the bath. Usually a bucket is used for the predissolving step. Two grams per liter is equal to 17 pounds of dispersant per 1,000 gallons of solution. When adding the predissolved dispersant to the bath make sure adequate agitation is used and make sure the dispersant is evenly distributed in the bath before the next step.

5. Predissolve the nickel acetate (2 g/L) in deionized water as above and add to the bath with agitation.
6. With good agitation, slowly raise the pH to 6.8 with dilute (10% by volume) ammonium hydroxide.
7. Predissolve 1 g/L sodium acetate and add to bath. This will buffer the solution and prevent pH fluctuations, making control of the pre-seal much easier. Do not add sodium acetate until after the pH has been adjusted to 6.8 (Step 6).

The pre-seal is controlled by maintaining proper pH, nickel acetate and dispersant levels. Adjustment of pH is made with acetic acid or 10% (by volume) ammonium hydroxide. Nickel acetate is monitored by titrating Ni(II) with EDTA. It is assumed that consumption of nickel acetate and dispersant will be equal, therefore equal amounts of nickel acetate and dispersant are added to adjust the concentrations.

As solids build up in the bath due to pH adjustment, drag-in from preceding tanks and the addition and evaporation of makeup water, sealing smut becomes harder to control. The dispersant concentration will probably have to be increased to help prevent smut. The concentration should be increased before severe smut problems develop. Once severe smutting begins, it is extremely hard to stop, yet proper dispersant levels are effective in preventing smut initially.

Also important in preventing sealing smut and obtaining a quality seal is thorough rinsing after the pre-seal tank to prevent carry-over of nickel acetate and dispersant into the final seal tank.

After pre-sealing, the anodic film is ready for the final seal. Hot water, nickel acetate, or potassium dichromate may be used for the final seal.

Hot Water Seal

The hot water seal has the widest acceptance of any seal system in the industry. Properly maintained, it is capable of producing a high quality seal. It is comparatively easy to maintain and produces minimal water pollution problems.

TABLE 10: Hot Water Seal Process Conditions

	Recommended
Water	D.I. preferred
pH	5.5–6.5
Temperature	203–212°F/95–100°C
Time	Depends on coating thickness and pore diameter
Phosphate	2–3 ppm
Silica	less than 5 ppm

Nickel Acetate Seal

A final seal containing nickel acetate is required for some automotive and dye applications. The final nickel acetate seal provides slightly better performance in FACT and ADT tests, and is more resistant to phosphate contamination than the final hot water seal. Recommended operating conditions are as follows:

TABLE 11: Nickel Acetate Seal Process Conditions

	Recommended
pH	5.0–6.0
Nickel Acetate	5.0–5.8 g/L
Temperature	176–194°F/80–90°C
Time	15–20 minutes
Phosphate	2.5–20 ppm
Water	D.I. or tap water

As in the pre-seal and hot water seal, proper rinsing and proper agitation are essential. Continuous filtration should also be provided for the nickel acetate final seal to remove any precipitated nickel or aluminum hydroxide. Filtration has been shown to increase seal life by up to 50%.

Seal Problems

There are many “unknowns” that can interfere with hot water or modified hot water sealing. However, in most cases the problem can be solved by simply considering the four most common problems encountered: *LOW pH, LOW TEMPERATURE, HIGH PHOSPHATE, and HIGH SILICA.*

pH (Acidity – Alkalinity)

To gain a better understanding of pH, obtain a descriptive booklet from a manufacturer of pH equipment. A good pH meter is essential; pH papers are not accurate enough for checking seal solutions. Meters should be standardized with known buffers at pH 4.0 and pH 7.0. Standardization with a single buffer at pH 7.0 is not satisfactory because variation may occur in the lower range. Read the instructions with the meter; pH meters often “drift” or do not hold constant.

pH meters are delicate and should be treated with care. A good bench model mounted on a stable, vibration-free bench in a non-corrosive atmosphere is recommended.

Every effort should be made to avoid checking the pH of hot solutions (180–210°F)/(82–99°C). Although this is theoretically possible, we have not encountered a case where accurate pH's were obtained on hot solutions. Temperature compensation is provided with most pH meters but it compensates only for electrode potential changes with temperature and not for the actual solution pH changes. All solutions change pH as the temperature changes, and all recommended operating ranges are based on the pH at 70–80°F/21–27°C. Since this is such an important factor in sealing, the sample should be cooled to 80°F/27°C before taking a reading. It is also difficult to check the pH of a new seal bath of deionized water because of lack of ions in solution to activate the meter.

A rapid decrease in pH is an indication of poor rinsing resulting in sulfuric acid and phosphoric acid contamination being carried into the seal. Good rinsing results from an adequate number of rinse tanks, ample water flow, proper drain time and sequence of processing. The final rinse before each seal tank must be a well-agitated D.I. rinse. Carrier bars or conductor bars should be rinsed after Bright Dipping and again after anodizing to wash off acids that will later drip into the seal bath due to condensation of hot water vapor on the bar during sealing.

When designing racks, avoid a design that could trap acid solution (especially Bright Dip which is difficult to rinse) between various flat sections or in pockets. Parts should be racked to rinse and drain properly.

The pH of all seal tanks should be measured and adjustments made on a regular basis, preferably every two hours. Wide fluctuations in pH will adversely affect seal quality. At high pH's (usually above 7.0) the appearance of smut becomes a problem. At pH's less than 4.5, no sealing takes place at all. When adjusting the pH upwards, always dilute the ammonium hydroxide with water before adding to the bath to avoid the formation of solids due to localized areas of high pH. Ammonia adjustments to nickel acetate or pre-seal tanks should also be made slowly to prevent precipitation of nickel hydroxide at the point of addition.

Temperature

A minimum temperature of 203°F/95°C is recommended for a hot water seal. This solution should be operated near boiling. Often people are not aware of the exact temperature of the seal. Many depend upon steam pressure gauges and temperature gauges which are often inaccurate.

Always insist that the temperature of the seal be checked with an *accurate non-mercury glass thermometer*. Often, dial reading, stainless steel pocket thermometers are used, but these become inaccurate from rough handling.

It is recommended that the seal be equipped with some form of mechanical agitation because it is possible to have varying temperature in the tank due to placement of the steam coils or stratification of water at different levels. Mechanical agitation in the seal is far superior to air agitation which is effective only in the top one-third of the bath. The use of air agitation may cause a continual decrease in pH due to the absorption of carbon dioxide (CO₂) from the input air, thus forming carbonic acid. Air from low pressure blowers is recommended. Compressed air must not be used because air from compressors carries compressor oils which can leave a smut-like film on the part.

Phosphates

In general, 10 ppm phosphate is the recommended maximum concentration allowable. "Poor" sealing will occur at higher concentrations, although the anodizing specifications of at least one automotive manufacturer sets 5 ppm as the maximum acceptable limit for phosphates in a hot water seal. Phosphate contamination can be controlled only by thorough rinsing before and after the anodizing step to eliminate or reduce the "drag-in" of phosphoric acid Bright Dip solution to the anodize tank and from the anodize solution to the seal tank.

Every laboratory should be equipped with and use a phosphate test kit. Approximately 50% of all the sealing problems are due to phosphate contamination. The FACT Test is quite sensitive to phosphate contamination and seals cannot be operated with much more than 7 ppm of phosphate and consistently pass the FACT test.

The need for small amounts of phosphate (2–3 ppm) in the seal has been proven. This concentration helps to decrease smut formation. To maintain 2–3 ppm phosphate in a new D.I. seal bath, 7.5 ml of 85% reagent grade H₃PO₄ should be added for every 1,000 gallons of seal solution. This should be monitored by a phosphate test kit. For further information on the effects of phosphate in the seal, contact PCS Sales Technical Service.

Silica

Silica contamination above 5 ppm will hinder sealing and result in poor values on corrosion tests. The dye stain test cannot be passed with silica levels above 10 ppm which indicates no sealing at all.

Silica may be found in the tap water supply and can also enter the seal solution from a deionizer. Silica is an extremely weak acid and will not register on the conductivity meters of the deionizing unit. As the resins become saturated, the stronger acids displace silica which goes into the output deionized water, either to the seal tank or storage tank.

There are special instruments capable of detecting silica, but in most cases to prevent “silica breakthrough,” it is necessary to regenerate the ion exchange resin before the standard conductivity instruments indicate a need for regeneration. This can be controlled by installing water meters on the line to the deionizer. Operating experience will establish the maximum amount of water that can be deionized before the “silica breakthrough point” is reached.

Close monitoring of silica in seal tanks is mandatory. A regular dumping schedule should be established to maintain a high quality seal at all times. Silica test kits are an inexpensive and easy method for determining silica levels in both the seal tank and the deionized water.

Smutting

Much has been written about “smutting” or “chalking” in the seal tank. Smutting refers to the deposit of a foreign substance on the part during sealing which can affect the appearance or the adhesion of subsequent coatings. There are a number of different types of sealing smut. Frequently, the type of smut present is difficult to determine. The following are a few of the most common.

- a) *Aluminum Sulfate* — Approximately 95% of all smutting problems are caused by poor rinsing after anodizing, resulting in aluminum sulfate contamination of the first seal tank. Aluminum sulfate is insoluble above a pH of 4.5, with a minimum solubility at approximately 5.7. It is always present in the seal tank as a dispersed solid which can be deposited on the parts. The aluminum sulfate precipitate is always powdery and can be removed easily by wiping the parts. It does not smear or feel sticky unless there is also a substantial amount of phosphate present.
- b) *Nickel Acetate* — All nickel acetate seals and pre-seals leave a small amount of nickel hydroxide on the surface of the part. Nickel acetate smut can also form when parts are rinsed in an acidic rinse immediately after the pre-seal. If the rinse pH is below 5.5–6.0, the nickel can be leached from the pores and deposited as nickel hydroxide on the surface of the part. These deposits can be heavy enough to be seen as a powder, and will interfere with paint adhesion. All parts to be painted should be rinsed in a hot D.I. rinse (pH 6–7) after a nickel acetate pre-seal. As with aluminum sulfate, nickel acetate smut is always powdery and easily removed, unless the bath is also contaminated with large amounts of phosphate.
- c) *High Phosphate* — High phosphates cause two smut-related problems, especially when the pre-seal is used. First, aluminum and nickel phosphates are less soluble than their sulfates, therefore, they are more likely to precipitate in high phosphate baths. Second, phosphates inhibit sealing, so the nickel deposited in the pores during the pre-seal is leached out during the final seal. This type of smut may not be visible until the part is touched, and then the surface will “smear.” The smut tends to get worse as the surface is rubbed, and cannot be removed.
- d) *Low Phosphate* — Although the mechanism is unclear, seal baths with no phosphate at all produce a coating which smears when touched even though it is well sealed. The smears or streaks cannot be completely removed. All seal baths should have at least 2.0 ppm phosphate.
- e) *Hard Water* — Tap water frequently contains contaminants that make it unacceptable for sealing. High levels of calcium and magnesium can cause a powdery, easily removed smut due to their precipitation as sulfates. Minimum makeup water quality for acceptable sealing and bath life is as shown in table 12, p. 43.

- f) *Dispersant* — The use of dispersants or wetting agents in the final seal is of questionable value and should be avoided. Frequently these will be left on the surface of the part as a clear film which smears or feels sticky when touched. Residual dispersant or wetting agent prevents adhesion of paint or vinyl to the part, therefore, it cannot be tolerated on most automotive lines. Compressor oil coats the parts much like a dispersant or wetting agent in the final seal, therefore, compressed air should never be used for seal agitation. Always use low pressure blown air.

TABLE 12: Maximum Limits of Contaminants

	Bath	Makeup Water
Silica	5–10 ppm	0.5 ppm
Phosphate	10 ppm	2 ppm
Hardness	15 grains	1 grain
Sulfate	50–100 ppm	0 ppm
Chloride	100 ppm	10 ppm
Flouride	5 ppm	0.5 ppm



1101 Skokie Blvd., Northbrook, IL 60062
www.nutrien.com