THE FIRST TEN MINUTES

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A practical review of process procedures and ramping techniques for hard anodizing in aerospace applications. The presentation will center around the early portion of the ramp cycle as a key factor for better quality anodize with more efficient use of electrical power. The critical importance of the first few minutes of the anodize run will be discussed and explained with special applications and real-life examples

INTRODUCTION

Modern applications of the hard anodic film, especially in aerospace applications, are extremely demanding of the processor in several ways. These include but in no way are limited to:

-Exotic alloys.

-Tighter dimensional tolerances, including coating to final dimension.

-Multiple finishes on a single part.

-Tight, difficult-to-coat areas within complex parts. Often these may require auxiliary cathodes, pumps, hidden contact points etc.

Overriding all of this is the economic pressure to run a profitable operation. We must run sufficient load densities to be profitable while developing procedures that meet all requirements for these full loads. We must avoid process failures because rework is rarely allowed due to dimensional issues.

It behooves the hard anodizer to develop a strong procedure for racking and running hard anodize work. Of particular importance to us here today is what happens at the outset and actually, before we even put parts in the tank.

The goal of this paper is to lay out some basic ramping procedures which have been proven to be workable in aerospace hardcoating scenarios.

Notes:

Aerospace work is always done to a specification. Military Specs, such as Mil-A-8625, do not dictate process procedures whereas Prime Aerospace specs such as PS13208 often lay out exact chemistries, ramping and running procedures. To further complicate issues, a Processor can often substitute their own procedure for a Prime Spec procedure given that Primes' approval.

In this paper, we shall assume that the processor has discretion in choosing the Process parameters and procedure.

The procedures presented herein are solely for reference only. They represent procedures that have been successfully used in one aerospace hardcoating facility. Any application of the procedures outlined in this paper is solely at the discretion of and is solely the responsibility of the processor.

BASIC SYSTEM REQUIREMENTS

In order for proper procedures to work their best, they must be supported by a quality hard anodize system. The details of this go far beyond the scope of this paper but some basic requirements would be:

- Vigorous solution agitation to maintain temperature uniformity and to permit proper cooling of the load during processing. Air, if used, must be clean and oil free.
- Refrigeration and controls sufficient to maintain temperature within +/- 2 Deg F
- Rectifier with sufficient capacity to deliver the required current at the maximum anticipated load area and voltage.
- All meters should be calibrated and accurate to within +/- 3% of full scale.
- Cathode area sized appropriately to load areas. Bussing resistance balanced across tank.
- A quality anodizing additive is highly recommended. The catalyzed endothermic reaction which a proper additive supplies is invaluable.

PREPARATION

Once the load has been racked, it must be presented to the tank in such a way that the resistance is approximately equal to all parts in the load. Resistance will never be equal but differences can be minimized through some basic racking good practices.

All racks for the same part in same run must be identical. Having 4 single aluminum splines and 2 single titanium splines will result in the parts on the aluminum splines being over coated relative to the titanium splines.

Typically, splines on the ends of the bar, closest to the copper landing pads, tend to receive a disproportionate amount of current. This is because resistance is lower at this point. Racking procedures should be developed which take this into account. Dummy panels at the ends of the flight bar are a common method of limiting excess current to parts at the end of the bar. One possible technique which we are beginning to research would be using different materials of varying resistance for the rack components. This is promising but still remains to be tested in production scenarios.

Regardless of the exact racking technique used, the goal is to minimize and balance resistance across the entire load.

INITIAL ACTIVATION

The first step begins the Activation Phase[i]. During this phase the barrier layer is formed. After a certain critical thickness is formed, micro-pores begin to develop. There is evidence from radio-chemical tracer studies done by Bruce and Baker [ii] that this corresponds to an initial period of instability in the process of penetration of the sulfate ions before equilibrium is established.

This initial instability can be observed at the ammeter, during the early stages of the run. Typically, during the first few minutes, as the voltage is increased, the current will spike up and then quickly drop down. This initial amperage drop off must be allowed to occur so as to encourage a more even coating formation over the entire load. In essence, you need to wait until the electric field across the load/associated with each pore is approximately equal before increasing the voltage.

The implications of the above are far-reaching. This means that it will take some time (usually between 1-3 minutes) until the initial activation set point is reached. It also means that a ramp which allows the electric field across the load to stabilize at a given energy level before increasing the electromotive force accurately reflects what is actually occurring during coating formation.

Ramp: The raising of voltage or current from a base setting to a final running voltage or current density over a set time period.

A basic ramp pattern for 6061 might be as simple as:

Immerse parts in tank under 2V

Manually increase Voltage to 10 ASF over 1-3 minutes. Manually gradually increase voltage between each stage. Go in as small increments as is practical.

3-5 min 10 ASF

3 min 15 ASF

3 min 20 ASF

3 min 25 ASF

30 ASF run until end

This basic ramp works very well on easily coated alloys such as 5052 or 6061. Typically, for a 1000 amp load of 6061 at 32F, 10 ASF will be reached between 15-20 volts. It could take anywhere from 1-3 minutes to reach this initial set point. More discrete parts in the load tend to increase the time required for a ramp to initial activation. Part geometry and rack design will also affect this.

If the initial voltage is increased too quickly, the odds of thickness variance within the load increase.

This is because the parts with lower resistance due to positioning on the rack and within the tank itself will begin coating faster than those with greater resistance. If we take time building the initial barrier layer and pore structure and allow the entire load to stabilize at a given energy level before increasing the voltage we will minimize the variance within the load.

Also, since pore diameter is indirectly proportional to voltage, a higher voltage at the outset will limit us at the end of the run because the initial pores formed will be too small to allow current down to the base of the pore without excessive voltage once the coating begins to grow thicker. This could result in either a soft coating or insufficient thickness due to the rectifier running out of voltage. Thus we could say that:

Higher initial voltages limit maximum final coating thickness.

These first few minutes truly are the most critical part of the cycle. Due to the fact that the anodic film progresses inward, the initial pore structure developed will either facilitate or hinder the balance of the process. This is the key point of this entire presentation. The processor must realize this fact and its implications. A proper ramp, along with specific procedures for the different alloy groups greatly increases the odds of success.

A real life implication of these “first 10 minutes” was experienced recently: An 800 amp load of 6061 cylinders was racked on racks that were of borderline capacity for the load. The initial activation phase of 10 ASF took over 22 volts to achieve. The load was ramped for 12 minutes at which point the operator decided to pull the load and increase it’s ampacity by adding additional vertical splines. Due to the fact that the initial pore structure had already been established at the high voltage, the load required 59 Volts to complete whereas it normally should have required from 45-50 V.

Despite switching to a better rack, the fact that the initial pore structure was tight (due to the high voltage required to drive 10 ASF through smaller racks) negatively impacted the balance of the run.

The mechanism of anodic film formation is such that initial pore structure and process parameters have significant, sometimes overriding, effects upon the entirety of the run.

It is quite possible to develop a pore structure at the outset which will make it practically impossible to achieve thicker coatings, especially on the more difficult alloys. This is why the first few minutes are the most critical.

DWELL TIMES

A proper ramping procedure takes the mechanism of coating formation into account. The concept is to gradually increase the voltage (or the amperage in the voltage mode) until our eventual current density is reached. We also want to maximize the coating time at each energy level applied to the load while taking specific alloy reactions into account so as to ensure that all varying areas of resistance have been coated and the resistance variation minimized across the load. Old-School hard anodizers refer to this as “filling in”.

This brings us to the subject of dwell times. A typical ramp out of the box is a linear ramp over time. For example: a ramp from 0-16 V over 5 mins. Such a ramp, while attractive from a programmers’ point of view, does not take the mechanism of coating formation into account. It would tend to increase voltage faster than the maximum rate at which the entire load could be evenly brought up. Parts anodized in this manner might require more voltage to achieve final thickness and the load might have greater thickness variation between the high and low parts.

If we pause ramping to allow the load to dwell at certain current densities along the way we will give the slower coating parts a little more of an opportunity to coat before we increase the voltage. Typically 3-7 dwell steps are used[iii]. In the example earlier, there were 4 dwell steps prior to the final setting.

In a dwell stage the amperage is set at the outset and not touched. The amperes will tend to drop off as the coating thickness and therefore resistance increases. This drop off should be allowed to occur to a maximum of approximately 10% before manually raising the voltage to bring the amps back in range.

PULSE

Pulsing the voltage during the initial activation phase assist the formation of an even thickness across the load. Slow pulses of 0.5-2.0 seconds assist in activating the anode surface and have the beneficial effect of initiating coating formation at lower voltages. As stated earlier, limiting voltage at the outset of the run is critical.

Pulsing can be set so that the load pulses from a lower voltage back up to the set point voltage. Such a “bottom up” pulse is safer from high spikes and provides all of the beneficial effects described above.

BASIC RAMPING REVIEW

1. These first few minutes are the most important part of the cycle. Due to the fact that the anodic film progresses inward, the initial pore structure developed will either facilitate or hinder the balance of the process.
2. Limiting Voltage at the outset is critical.
3. Ramping up to initial Activation Phase (8-10 ASF) should be done gradually, from 1-3 minutes is typical.
4. 3-7 Dwell points along the way to final running current density. Each dwell typically 3 minutes
5. Pulsing during Initial Activation Phase assists in even coating formation.

OTHER ALLOYS

The basic concepts described above apply to all alloys. Modifications are made to the procedures that take into account the alloy being coated. The two most common “aerospace alloys”, 2024 and 7075 are the next step.

2024 (High Copper)

2024 is the alloy that separates the basic hardcoater from the more advanced one. Case in point, there are actually several hard anodize facilities that are approved for 6061 hardcoat only and not 2024 by Boeing and other Primes. Due to the high copper content of this alloy it is more easily burned than 6061 and requires more voltage to achieve the same current density. Hardcoaters know that 2024 coats slower than 6061 due to this.

The ramp for 2024 must be slower and more gradual than that for 6061. There are aerospace Prime hard anodize specifications which call out 50 minute ramps for 2xxx series alloys. Such a ramp, while it will tend to produce softer coating, will be relatively safe to run and will also have the benefit of producing a tight thickness range between the parts in the load. The specification which calls out this process has a thickness requirement of .002” +/- 10%. For point of reference, The Military Specification Mil-A-8625 has a thickness requirement of .002” +/- 20%.

Here is a possible 2024 ramp:

Immerse parts in tank under 2-3V (if possible)

Manually increase Voltage to 10 ASF over 1-3 minutes.

5 min 10 ASF (Pulse ON)

Slow Pulse-Step-Ramp to 15 ASF over 2-4 minutes

5-10 min @ 15 ASF (Pulse OFF)

2 min @ 18.75 ASF

2 min @ 22.5 ASF

2 min @ 26.25 ASF

To End: 100% RCD (30 ASF)

Key Aspects of this ramp are:

Initial Activation Phase of 5 min 10 ASF with Pulse ON. “Bottom Up” Slow Pulsing has been used successfully.

Long Dwell Time of 5-10 min at 50% of final current density without pulse

Long ramp up to final current density. Several discrete dwell periods of 2 mins each.

Please note that these times are for the dwell periods only and do not take the time required to ramp up between stages into account. As stated throughout, ramping should always be done gradually.

7075 (High Zinc)

The ramping techniques for 7075 take into account the sensitivity of this alloy to chemical attack. It is also highly recommended that the time between deoxidation and initial application of current in the anodizing bath be kept to a minimum.

Colder temperatures (30-32 F) are recommended for 7xxx alloys due to their susceptibility to chemical attack.

Here is a possible 7075 ramp:

Immerse parts in tank under 2-3V (if possible)

Manually increase Voltage to 10 ASF over 1-3 minutes.

3-5 min 10 ASF (Pulse ON)

Slow Pulse-Step-Ramp to 15 ASF over 1-2 minutes

3-5 min @ 15 ASF (Pulse OFF)

2 min @ 20 ASF

2 min @ 25 ASF

To End: 100% RCD

Key Aspects of this ramp are:

Shorter Initial Activation Phase of 3-5 min 10 ASF with Pulse ON.

Shorter Dwell Time of 3-5 min at 50% of final current density without pulse

Shorter ramp up to final current density.

COATING RATES AND THE "720 RULE" CONFUSION

Different alloys coat at different rates. More precisely put: Different alloys require different voltages in order to reach the same current density.

There are many charts available which show the voltages required to reach 12 ASF for different alloys given the same processing parameters. These charts have limited value to the hard anodizer as he/she will be typically anodizing at a significantly higher rate than 12 ASF.

Since film thickness is proportional to current x time (or coulombs passed), what would be more critical for the hardcoater would be to determine the coating rates in terms of amp-hours or amp-minutes for the alloy groups.

A known area of an alloy should be coated at a known current for a period of time. From those results, the coating rate can be determined. Alternatively, a calibrated amp-hr meter could be used. This should be done with all of the main alloy groups.

In our facility we have found the following:

6061: 720 amp/mins per sf = .001"

7075: 560 amp/mins per sf = .001"

2024: 810 amp/mins per sf = .001"

I would highly recommend doing your own calculations in your own system. There is wide variance in published studies. For example, Brace lists 7000 series alloys as "group 2" which he claims requires 900 amp mins/sf [iv] to reach 1 mil. This number represents an approximately 60% slower rate of coating formation observed by Brace as opposed to what we see every day.. Brace's numbers are based off of earlier studies and his extrapolation from the data observed in those studies. His numbers are not the result of direct observation. The numbers given above are based off of years of direct observation of the aforementioned alloys in hard anodize production scenarios.

While it is true that the rate of metal deposited at the cathode or dissolved at the anode is proportional to the coulombs passed, there are obviously other factors influencing the coating rate of the differing alloys which cause the final number to differ from the number predicted solely by Faraday's law. With this enormous differential between established coating rates, the only safe way is to plot the rates for each alloy in each setup.

EXTENDED RAMPS

In addition to the basic ramping procedures described above, there are many cases in which an extended ramp is desirable. A ramp is typically extended by increasing the dwell time at each stage. Some of those cases could be:

1. Called out by Prime Spec: A Prime specification such as PS13208 lists out ramp times of over 40 minutes. In this case, the processor must hard anodize the parts per that spec unless a deviation has been approved. Actual Prime Specification Procedures will not be discussed due to their limited distribution.
2. Difficult alloys: For 2000 series including 2219, a longer ramp period of 18-30 minutes has been used successfully. This slow ramp is an excellent precaution to take against burning. It is also very workable for die Castings (High Si).
3. Difficult part configurations: Recessed areas require a slow ramp to ensure even current throw, sharp edges are easily burned unless the ramp is gradual.
4. Tight Final tolerances: In many cases, the final tolerance is only +/-.0002". In order for this tighter tolerance to be met on larger loads, the ramping must be extended. Also, final running current density may be reduced. Lower current densities improve accuracy of film thickness but at the expense of longer process times and possibly softer coatings.

POST HARDCOAT HONING

Very often, especially in critical aerospace applications, hardcoated parts are honed to a final dimension and surface finish. This presents a very unique opportunity for the application of ramping theory. For example, if a customer requires the inside diameter of a cylinder hardcoated while meeting extremely stringent dimensional and surface roughness requirements, the following process might be used:

1. Pre-hard anodize ID: 6.5322"-6.5326"
2. Coating thickness required: .0025" minimum.
3. Post Hone ID: 6.5309"-6.5311"

In this case, we know that after hard anodize, approximately .001" is going to be removed by the honing process. Extending the ramp so that you do not begin to approach higher current densities until after at possibly .0005" worth of coating is formed will greatly aid in coating thickness accuracy as well as allowing for lower final voltages at end of cycle (due to the larger pore structure that was developed at the outset). This may also allow the anodizer to run larger loads in some cases.

CONCLUSION

A proper ramping procedure is critical to achieving consistent excellent results in hard anodize. Limiting the voltage at the outset allows for a harder, smoother coating as well as a more accurate final thickness. Limiting the voltage at the outset will also reduce final voltage requirements, making larger loads possible.

By gradually activating the surface and then gradually, in a stepped pulse ramp, increasing the current over time in the voltage mode, we provide an even pore structure that extends all the way down to the base metal. This pore structure will facilitate thicker, even coatings with minimal energy waste.

Facilities should determine coating rates for all alloys under actual production conditions so as to accurately predict thickness.

“All the good or bad is done during the first few minutes of the run”

Fred Charles Schaedel

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[i] F.C Schaedel, proc NASF Sur/Fin 2011 The leading Edge to Top Quality Anodizing
[ii] Brace A. W., Baker H., Trans. IMF (1963) 40 P31
[iii] F.C Schaedel, proc NASF Sur/Fin 2011 The leading Edge to Top Quality Anodizing

[iv] Brace A, W. The Technology of Anodizing Aluminum p 159