Pulse Ramp Mixed Electrolyte Anodizing
Automated & Practical – All Aluminum and Titanium Alloys

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A new simplified practical system for pulse ramp technology using economical mixed electrolytes will be presented. Sulfuric acid concentrations in Type II and Type III anodizing tanks can be reduced by up to 50% with accelerated anodic coating formation rates. The electrolyte also has increased conductivity and promotes energy savings with operational ranges from 30˚ - 100˚ F. This technology will anodize all aluminum alloys, including 2011, 2024, 7050, 7178 and 380 DC at lower voltages with faster rates without powdering or burning. Data logger graphs will be presented along with production data. The paper covers commercial, military and aerospace applications.

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PULSE RAMP MIXED ELECTROLYTE ANODIZING
AUTOMATED & PRACTICAL
ALL ALUMINUM & TITANIUM ALLOYS

There are two new developments and major improvements presented in this paper. They definitely improve the quality and efficiency of all standard Type II Sulfuric and Type III Hard Anodize Systems while still operating within the existing parameters meeting and exceeding Commercial and Military Specifications. All data presented here is practical and can easily be integrated into any existing production system with very significant improvements in two specific areas.

QUALITY
EFFICIENCY

Let me give a little background leading up to the title and reason for this paper. Over the past 30-45 years, I have seen numerous times when the standard Type II and III anodizing processes just would not meet the specific customer requirements. Some of these requirements could be quite tough – even beyond the standard specifications. Since I was usually bound or forced to operate within existing specifications (Mil-A-8625), we therefore, in most cases, made process modifications and improvements in two areas:

> <u>Basic Electrolyte Modification</u> – <u>Mixed Electrolyte</u>
> Sulfuric acid conc. was reduced from15% to as low as 5%
>   Strong Acid Reduced by over 50%
> Additives/Modifiers were added to the electrolyte:
>   Standard Additives (Mae type)
>   Modifiers: Hydroxy – Carboxylic Acids
>
> <u>Pulse Ramp Procedure</u>
>
> Pulse Ramp procedures were modified for the first 5-10 minutes early in the anodize cycle. After all, the anodizers who know me appreciate what I always preach – that is – most if not all of the good and the bad is done during the first 5-10 minutes early in the anodize run.

Finally, high tech specifications got more demanding along with commercial production requirements so accelerated that I was being forced and ordered, but not approved, to operate outside the envelope of Standard Mil Spec Type II and III anodizing.

Yes, I managed to produce harder, heavier, faster coatings while still maintaining microfinish. However, I found my modifications were slowly developing into a mixed electrolyte with Sulfuric acid still the primary acid only by basic molar concentration. My reaction modifiers (not additives) were becoming so active that small comparative additions proved to give superior results. The Pulse Ramp, in turn, was incorporated to work with the sulfuric acid and reaction modifiers early in the anodize process.

After the preceding background, I can now answer a most important question in two parts with a quick review.

***Why Pulse Ramp & Mixed Electrolytes at this time frame*?**

Part #1 – Mixed Electrolyte formulations produce anodized finishes of far superior quality and efficiency on a consistent basis not possible with Standard Type II and III formulations in production. Carboxylic acids and Special Hydroxy Poly–Carboxylic groups are very effective as mixed electrolyte modifiers when used with sulfuric acid as the primary electrolyte.

Part #2 – Pulse Ramp has always been beneficial historically but it is most important during the first 5-10 minutes of any anodize cycle. The quality and fate of the customer part is usually determined early in the process run.

Let us look at the complete spectrum approach, which I initiated about 20 years ago. That is how three different key areas are integrated to work together as one complete system.

Chemistry – Mixed Electrolytes
Electronics – Rectification – Half Wave Preferred
Auto Control – Pulse Ramp -Simplified and Practical
Low Voltage Cap/Shunt Discharge Preferred

Now let us move forward and present some Mixed Electrolyte formulations along with performance data and how this can be applied to the Type II and Type III anodize processes.

I – MIXED ELECTROLYTE SOLUTIONS
Basic Formulations
Performance Data

Basic Formulations

Mixed Electrolyte Formulations operating within Standard Type II and III Sulfuric Acid Parameters will be presented here. They have been formatted to give maximum performance in these areas.

Faster Anodize/Coating Rate
Superior Anodize Coatings (Wear & Micro Hardness)
Best Micro Finish along with Pore Structure
No Powder or Powder Burn

There are seven basic formulations to be presented which have been proven successful for anodizing aluminum and titanium. The first formulation is a combination of other formulations to give maximum efficiency.

MX#1 Sulfuric/Tartaric/Organic

Sulfuric Acid	9.0 – 14.5 % Vol (165 – 265g/l)
Tartaric Acid	1.5 – 3.0 % Wt/Vol
Lactic Acid	1.5 – 3.0 % Wt/Vol
Oxalic Acid	1.0 – 2.0 % Wt/Vol
Temp	30 – 50˚ F
Current Density	25 – 40 ASF

MX#2LS Low Sulfuric/Tartaric /Organic

Sulfuric Acid	6.0 – 10.0 % Vol (110 – 180 g/l)
Sodium Bisulfate	7.0 – 10.0 % Wt/Vol
Tartaric Acid	1.5 – 3.0 % Wt/Vol
Lactic Acid	1.5 – 3.0 % Vol
Oxalic Acid	1.0 – 2.0 % Wt/Vol
Orzan (Lignin)	0.25 – 0.50 %
Temp	30 – 50˚ F
Current Density	25 – 40 ASF

MX#3LS	**Type 23MX3 Mixed Electrolyte**	
	Sulfuric Acid	6.0 – 10.0 %Vol
	Sodium Bisulfate	7.0 – 10.0 % Wt/Vol
	Std Additive (Mae type)	4.0 – 6.5 % Vol
	((Alpha Hydroxyacetic Acid (70%)	2.4 – 3.8 % Vol))
	((Glycerin	1.6 – 2.7 % Vol))
	Temp	30 – 75˚ F
	Current Density	25 – 40 ASF
MX#4LS	**Type 23 MX4 Mixed Electrolyte**	
	Sulfuric Acid	6.0 – 10.0 % Vol
	Sodium Bisulfate	7.0 – 10.0 % Wt/Vol
	Tartaric Acid	1.5 – 3.0 % Wt/Vol
	Std Additive (MAE – EHA = 15 - 30%)	4.0 – 6.5 % Vol
	Temp	30 – 75˚ F
	Current Density	25 – 40 ASF
MX#5LS	**Type 23 MX5 (Alpha Hydroxy Activated ME Modifier/Powd)**	
	Sulfuric Acid	6.0 – 10.0 % Vol
	Sodium Bisulfate	7.0 – 10.0 % Wt/Vol
	AHXMEP-5 (EHA = 60 – 85%)	2.0 – 3.5% Wt/Vol
	Temp	30 - 85° F
	Current Density	25 – 75 ASF
MX#6LS	**Type 23 AHXMEP/Tartaric**	
	Sulfuric Acid	6.0 – 10.0 % Vol
	Sodium Bisulfate	7.0 – 10.0 % Wt/Vol
	Tartaric Acid	1.5 – 3.0 % Wt/Vol
	AHXMP-5	2.0 – 3.5 %
	Temp	30 – 85˚ F
	Current Density	25 – 75 ASF
MX#7LSSH	**Type 23 AHXMEP/SHA**	
	Sulfuric Acid	5.0 – 8.5 % Vol
	Sodium Bisulfate	5.0 – 8.5 % Wt/Vol
	AHXMP-5	3.0 – 6.0 % Wt/Vol
	Orzan (Lignin)	0.25 – 0.50%
	Temp	30 – 110˚ F
	Current Density	25 – 75 ASF

The seven mixed electrolytes listed here are all superior to the Standard Type II and Type III anodize formulations. The analysis and control is relatively simplified which will be presented later. However, most of the production work done for this paper was complied using formulations MX#4LS, MX#7LS and in particular MX#5LS.

The formulation MX#4LS uses a standard additive of the MAE type, which is very similar to most of the additives on the market. I have tested all of the available additives in the laboratory and in production. If these additives are used at their maximum concentration plus 20%, they will give fair to good results in a mixed electrolyte system. The formulations listed here will definitely give superior results over any Standard Type II – III sulfuric electrolyte.

The formulation MX#5LS uses a special new poly carboxylic acid combination modifier which I have formulated and tested over the last year in five anodize facilities. I am designating it as Code #AHXMP-5 (Alpha Hydroxy Activated Mixed Electrolyte Modifier Powder Dash 5). It has an endothermic heat activity in the pore structure 200 – 300% greater than all of the other additives and/or modifiers. I am listing it as a modifier because it is much too active to be called just another additive. The results at various test facilities indicate this material is also cost effective.

<u>Performance Data</u>
Specific for Mixed Electrolytes

I have found certain specific areas where mixed electrolytes will operate and perform well over expanded ranges and/or parameters outside the envelope for Standard Type II and III hard anodize passing all applicable specifications. You may have already noted some of the areas as follows:

***Primary Electrolyte Conc:**	**Reduced by 50%** 6 - 10 - 15% Vol.
*Temperature:	Expanded for Type II-III 30 – 50 – 70 – 85 – 100 - 125˚ F Type III Hard – Type II/23
*Current Density:	Expanded for all Types/Classes Type II 15 – 20 ASF Type III 25 – 30 – 45 – 75 ASF

Expanded operation ranges have many obvious advantages. These ranges/parameters can also be adjusted to produce various different finishes with superior quality on specific aluminum alloys.

There are many areas where the mixed electrolytes will operate and perform far superior to the Standard Type II and III basic electrolyte. Some of the areas that I have found more important to the aluminum anodizing industry are as follows:

- Manual and automatic control simplified
- Hard Anodize Type III and Sulfuric Anodize Type II Class 1 and 2 can both be performed in the same process tank meeting and exceeding all applicable specifications.
- Reduced process time – Faster Anodize Buildup
  Higher Current Density earlier in process run
- Harder Type III and Type II coatings.
- Better Microfinish (loss reduced during run).

- Quality Hard Bright Color Anodize – dyed
- Superior Quality when used with Two Step – Electro Color
  Remarkable Wear Resistance – All Alloys
- 2000 Series processed with no powder burning
  (2011, 2024, 2219 – examples)
- 7000 Series processed meeting all specifications
  (7075, 7050, 7178 – examples)
- Heavier Hard Coatings on Die Cast – 380
- Reduced Refrigeration
  (Endothermic Heat Absorption on Molecular Basis)
- Anodize Titanium Alloys
  All Applicable Alloys
  All Colors / Spectrum
  Better Abrasion Resistance

II. PULSE RAMP OPERATION AND PROCEDURE

Basic Pulse Ramp/Pulse Step Ramp

Pulse Step Ramp Plus CSD (Capacitance Shunt Discharge)

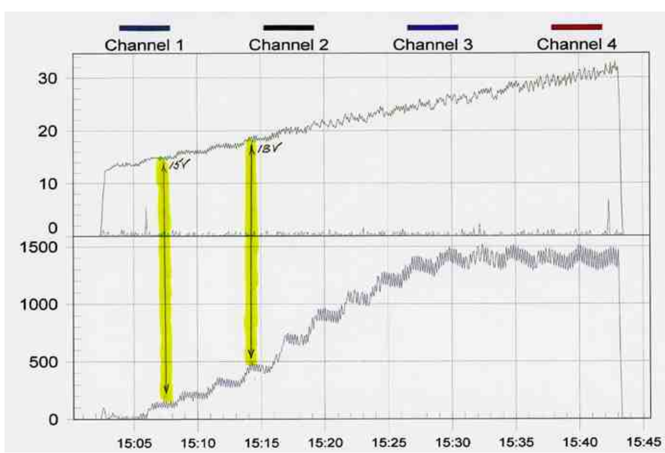
<u>Basic Pulse Ramp/Pulse Step Ramp</u>

Pulse and ramp are two areas of extreme importance for the production of quality Type II and III Anodize. I have also incorporated a dwell period into the system with ON Time and OFF Time. Therefore we really have a PULSE – STEP – RAMP. I can not over stress how PULSE – STEP – RAMP can really improve both your Type II and Type III anodize systems.

Pulse Step Ramp (PSR) actually works with the mixed electrolyte chemistry. Remember it is really important and should always be applied during the first 5 –10 minutes of the process cycle. Pulse Step Ramp or PSR as I shall refer to it in this paper improves the anodize coating in three particular areas:

1. Improves the initial 0.2 – 0.5 mil uniform buildup faster on all alloys.
2. Develops a pore structure which provides the basis for much brighter harder more attractive color anodize.
3. Develops a pore structure that will accept a better seal with superior corrosion resistance.

The Pulse Step Ramp is most effective when used with half wave rectifiers. However, it does work very well on Full Wave Rectification. Please note the example of a typical Pulse Step Ramp (PSR) cycle for Voltage and Current ramped to 1500 amps.

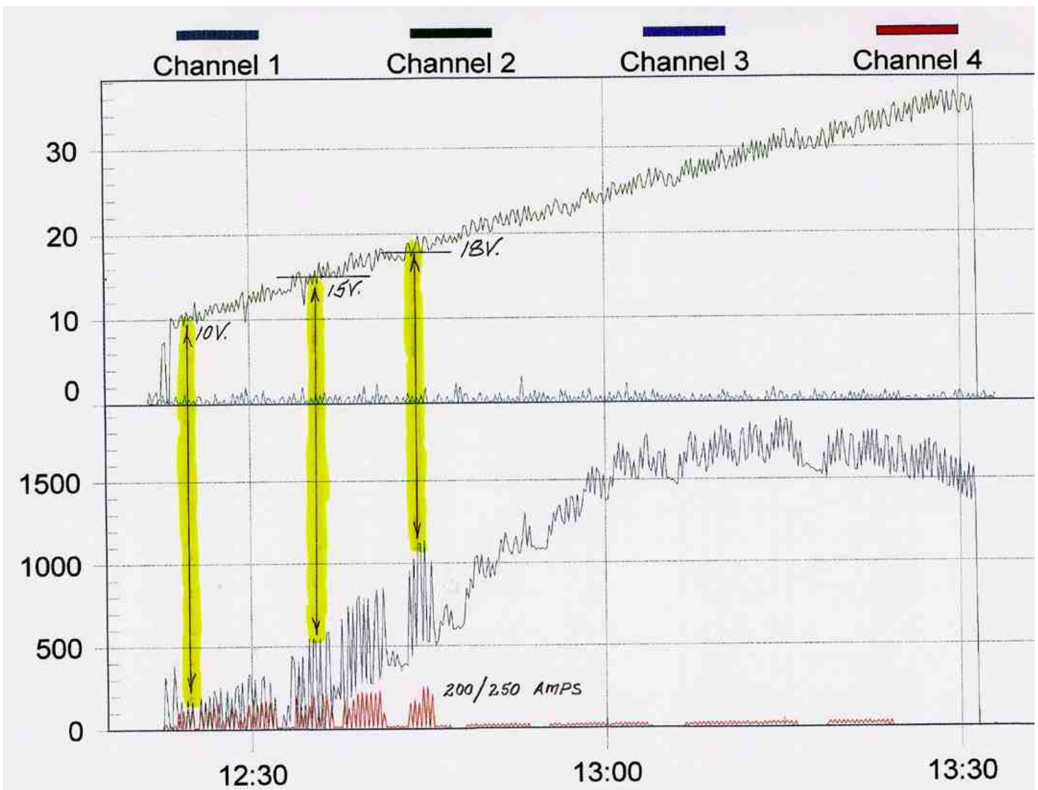


This example was taken from a production run of commercial parts requiring 2.0-2.5 mils hard anodize. The PSR was set for a step ramp with a one min dwell and one min ramp. Please note – all PSR operating specifications will be included in this paper.

Pulse Step Ramp Plus CSD (Capacitance Shunt Discharge)

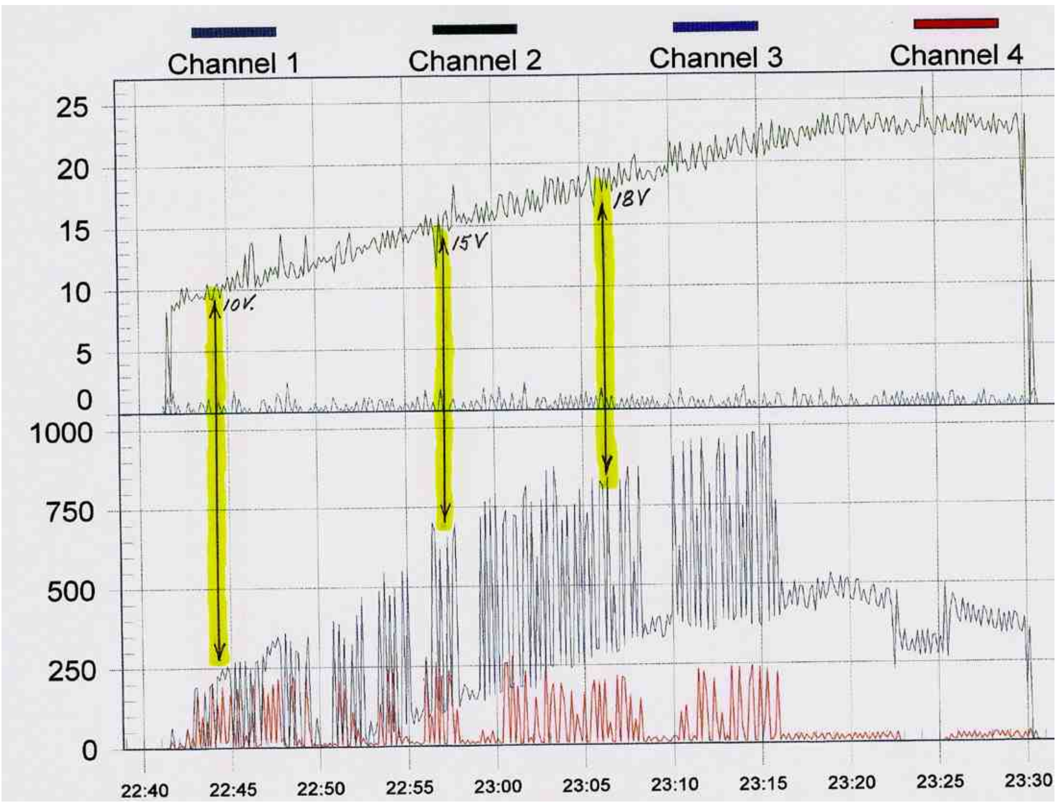
Now we will introduce a really important new development and improvement to the PSR System – Capacitance Shunt Discharge. We have used this system on half-wave rectifiers in the past very successfully.

However, now we can also use this unit on full-wave rectifiers, preferably secondary SCR. The following Anodize Pulse Ramp Dwell Cycle was run to 1500 amps with the addition of a capacitance shunt discharge unit.



Please note – we pull a higher amperage with CSD immediately at the start of the cycle initiating anodic coating formation before standard Type II and III anodize even begins. Check the current at 10 – 15 – 18 volts. At 18 volts we had a current loss of 200 – 250 amps. However, we had a current increase of from 500 to 1100 amps, which represents a net or actual current of 800 to 850amps on the production parts. This represents a very significant improvement in PSR Technology using CSD (Capacitance Shunt Discharge).

The CSD unit can be used in many different ways on various alloys and production loads depending upon its design as applied to specific rectifier capacities. The next graph represents one of many production loads run at one job shop production facility. This normally would have been a standard 500amp production run approximately one hour long due to racking, configuration and recessed areas on the parts. Also, please note time periods when the CSD unit was turned off to indicate the amperage change at the same voltage.



The Amperage gain is well over 50% in this extreme case as you can see from the turn off or interruption periods. There is always a small CSD unit that is operational during the entire anodize cycle with no pulse applied. You can note the amperage drop when this section is disconnected at 23:23 for 3 minutes. Please note – CSD specifications will also be included in this paper as they are integrated with the PSR technology.

III PROCESS PRODUCTION DOCUMENTATION

The following process data logger documentation has been confirmed in production at several facilities. Pulse ramp along with CSD was installed and used with the anodize rectifier when processing parts in mixed electrolytes conforming to those specified as MX #3LS through MX#6LS. The data logger records and other documentation in this section have been chosen as examples of how pulse ramp and mixed electrolytes work together efficiently to produce superior Type II and Type III anodize with respect to two specific areas:

1. The increased current (amperage) due to pulse ramp, PSR, and CSD at the beginning of the anodize cycle initiates a harder anodic coating with reduced process time.

2. The increased effective conductivity – due to mixed electrolytes and less free sulfuric acid – accepts the increased current density and further accelerates anodic coating buildup promoting amperage drop off (ADO) or amperage decay.

Data logger records also indicate the increased conductivity as it continues through the entire process cycle after reaching constant current density (CCD). This, of course, promotes better amperage drop off (ADO) which in turn increases anodic coating buildup and reduces anodize time.

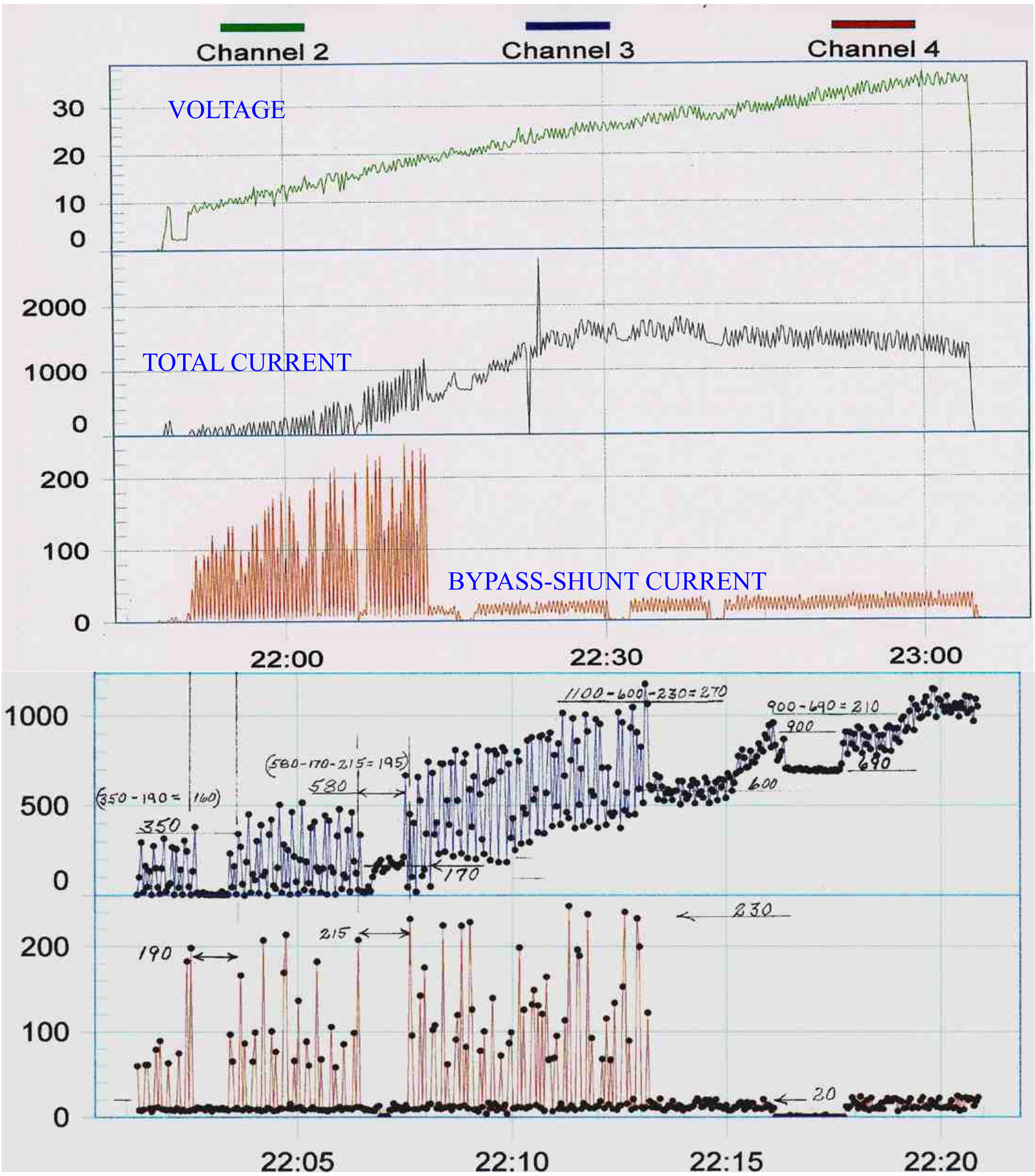
Data logger graphs III A-B-C-D were chosen to cover commercial and aerospace processing along with three different types of rectifiers. The rectifiers used were as follows:

III A – Full Wave/Secondary SCR's
III B – Half Wave/Secondary SCR's
III C – Half Wave/ Secondary SCR's
III D – Full Wave/Secondary Diodes

The results were good with both Full and Half Wave Secondary SCR rectifiers. However, Half Wave Secondary SCR is superior due to the 60cycle pulse. The Full Wave Secondary Diode rectifiers do not work well with the CSD system. However, with a new low resistance high inductance unit, we did see a much better amperage drop off (ADO) with mixed electrolytes. This, of course, does result in a faster anodic coating buildup, which is indicated in Graph III D.

III A-Production/Aerospace

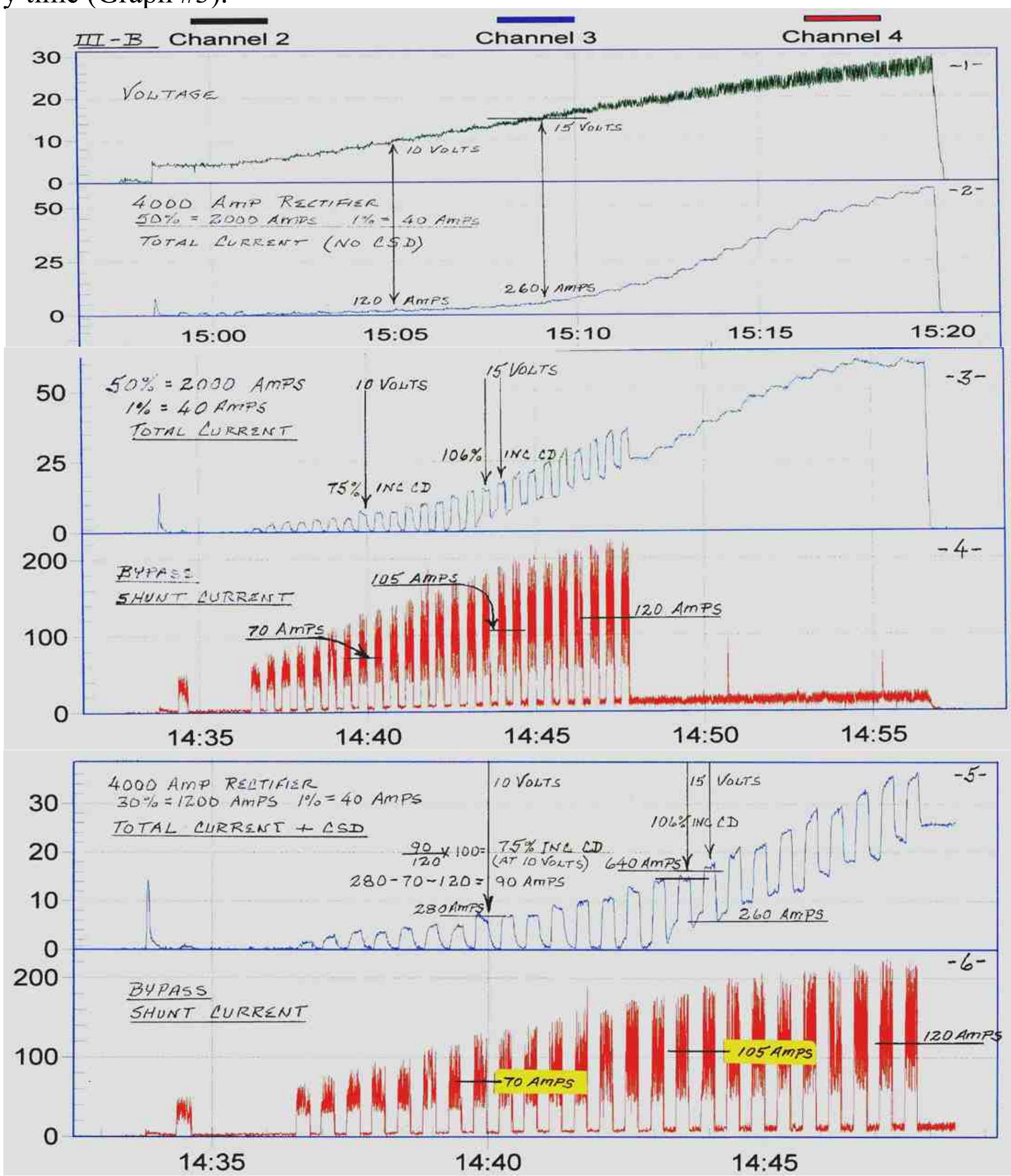
The following Anodize Production Load (1500 Amps) was recorded at one facility running aerospace parts. Ramp period 22:01-22:20 is expanded for evaluation. There is a net gain of 160 Amps at only 15 Volts non-existent without pulsed CSD with a bypass of 100-190 Amps.



Check the net gain of 195Amps at 22:07, which is a 115% increase above 170 Amps without CSD. Another net increase of 270 Amps or 45 % above 600 Amps is recorded at 22:13 (end of pulse ramp.)

III B – Pulse Step Ramp to 2500 Amps / CSD to 1500 Amps at 20 Volts

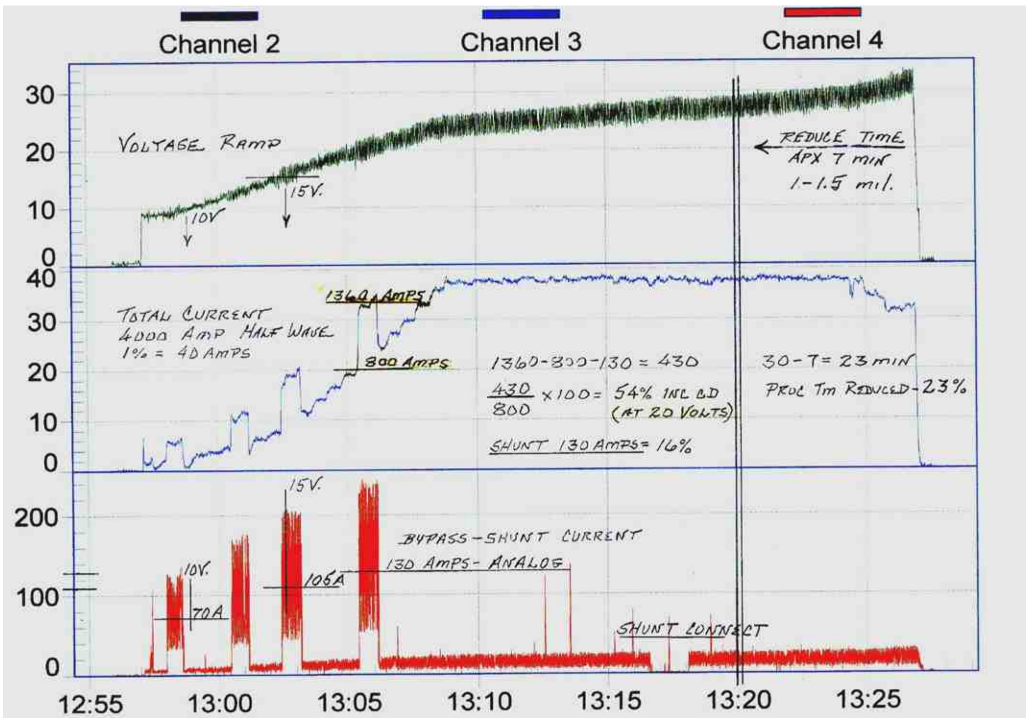
This pulse step ramp to 2500 amps represents one of the best ways to anodize in mixed electrolytes using capacitance shunt discharge. There are actually two identical process loads logged here. They were both pulse step ramped to 30 volts (Graph-1). The first load was run without CSD (Graph 2). The second was run with CSD pulsed at 10 second intervals on/off to allow for some recovery time (Graph #3).



Please note the 75% and 106% increase in current density at 10 and 15 volts respectfully (data logger graphs 3 and 5).

III C – Basic Anodize Run

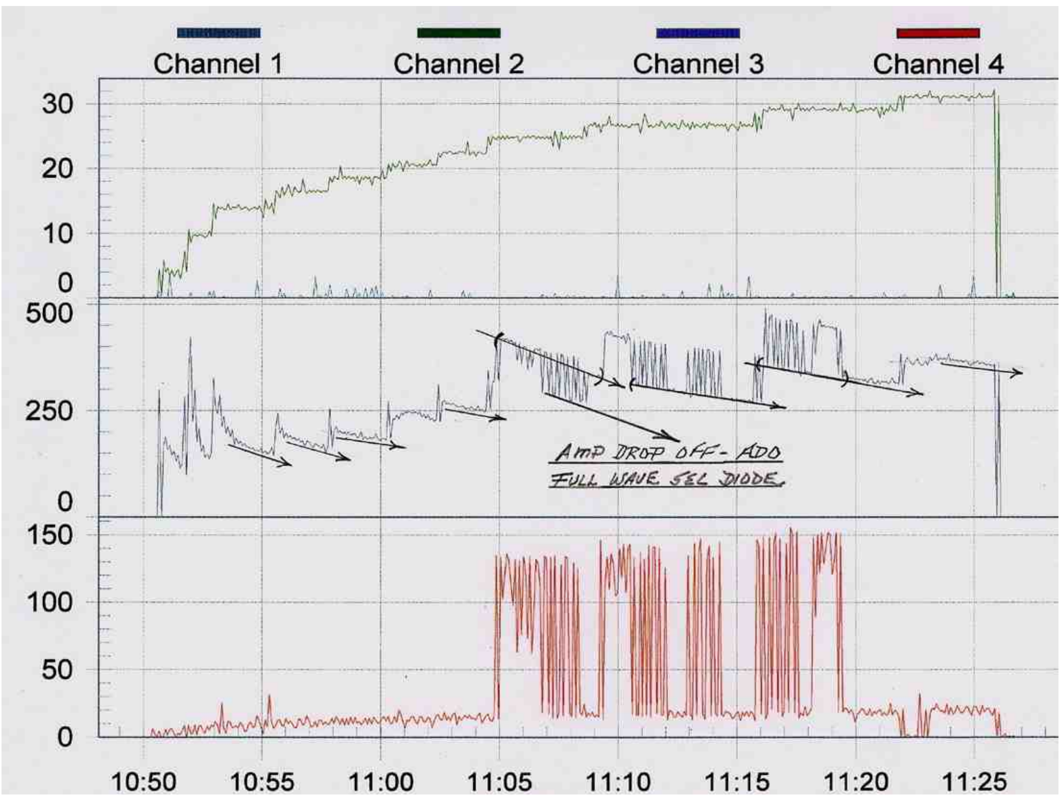
The following procedure is being used on all basic commercial alloys for anodize coatings up to 2.0 mils thick. The graph below represents one run when the load was ramped to 2000 amps (40-45 ASF) in 10 min. The mixed electrolyte temperature was maintained at 45˚ F to develop a standard hard anodize color. The total time was reduced by 23% to 21 min. for 1.3 mils.



Please check the net gain of 430 amps at 13:06 with a 54% increased current density using CSD. This same process cycle can be used on 2024 and 7075 passing Taber Abrasion requirements per MIL-A-8625 F.

III D-Anodizing with Full Wave Secondary Diode Rectifier

Full wave secondary rectifiers do improve anodize efficiency to some degree in one specific area – Amperage drop off (ADO) or amperage decay rate. Whenever amperage decay occurs at a faster rate, the anodic coating is almost always building up fast, becoming more dielectric, and requiring more voltage to return to constant running current density. The following graph indicates this ADO rate with a sharper amperage drop off angle as indicated beginning at 11:05, 11:10, and 11:16 respectfully when the CSD is engaged and pulsed. This was checked on several loads and found to repeat itself to a more marked degree when the CSD was connected and/or pulsed.

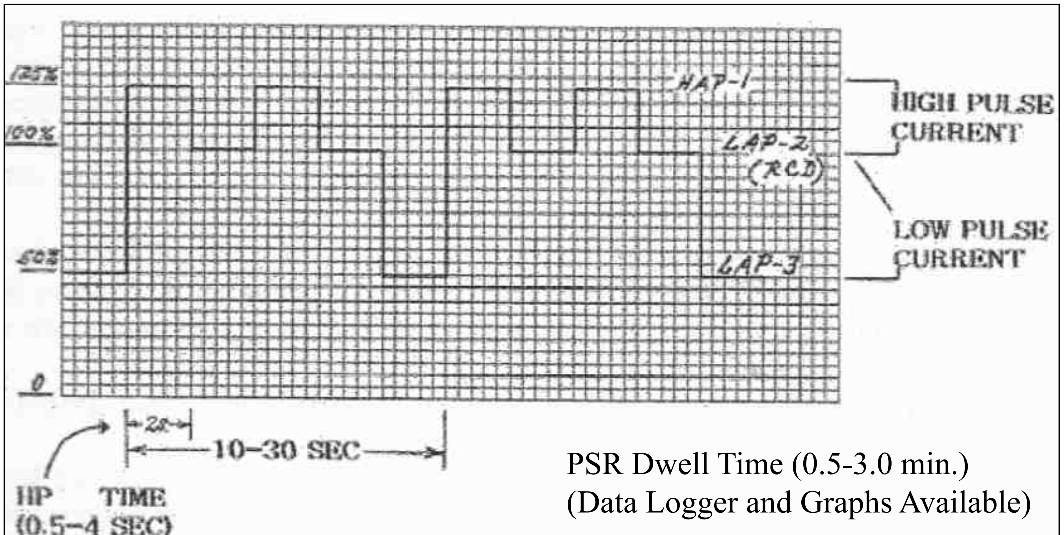


The amperage drop off (ADO) rate is increased to such a considerable degree that it is enough to be a significant improvement for the process cycle. Anodize operators know that faster amperage decay can be beneficial when running 2000 series alloys like 2024.

IV SPECIFICATIONS

<u>Pulse Ramp Specifications</u>

The pulse ramp operating specifications are all centered around slow high and low pulse times so that we can take advantage of the <u>Relaxation</u> and <u>Recovery</u> <u>Times</u> as they are integrated with the mixed electrolyte chemistry. The process load should also be started or manually ramped to 10-20% of the final total running current density (within 1-1.5 min) before a standard ramp is continued according to the following graph and specifications.
PSR Dwell Time (0.5-3.0 min.
(Data Logger and Graphs Available)



PSR Dwell Time (0.5-3.0 min.)
(Data Logger and Graphs Available)

Pulse Time Cycle/Duration	10 – 30 sec
HP - High Pulse Specifications	
HP – On Time	0.5 – 4.0 sec
LP – Off Time	0.5 – 4.0 sec
HP Current	10-25-50% Above Operating Amps (During Ramp Period)
LP - Low Pulse Specifications	
LP – On Time	0.5 – 4.0 sec
LP – Off Time	Total HP Time Cycle
LP – Current	25 – 50 % Below Operating Current

PSR - Pulse Step Ramp Specifications

PSR – On Time (Dwell)	0.5 – 30 Min
PSR – Off Time	Total HP/LP Time Cycle

<u>CSD – Capacitance Shunt Discharge Specifications</u>

<u>500 – 3000 Amp Rectifier</u>

CSD Ramped with HP (on Cycle)	0 – 20 Volts Max
CSD Bypass Current	100 – 300 Amps
(Parallel 15 1.0 OHM Inductive Resistors)	

<u>3000 – 6000 Amp Rectifier</u>

CSD Ramped with HP (On Cycle	0-20 Volts Max
CSD Bypass Current	300 – 600 Amps
(Parallel 30 1.0 OHM Inductive Resistors)	

V. CONCLUSIONS

- Low Sulfuric Mixed Electrolytes will produce superior quality anodize on a consistent basis where Standard Type II and III Electrolytes will not meet the requirements necessary for present and future Commercial and Military production.

- Low Sulfuric Mixed Electrolytes will reduce anodize tank time with better production. Due to increased effective conductivity in the pore structure.

- Superior Quality Anodic Coatings can be produced on all aluminum alloys with no powder or burning. This includes Alloys 2011, 2024, 2219, 7075, 7050, and 7178.

- Aluminum Casting Alloys including 380 Die Cast can be anodized in mixed electrolytes with improved hardness and micro finish.

- Pulse Ramp and Pulse Step Ramp should be used with all Mixed Electrolytes for fast formation of the initial 0.3 – 0.5 mil coating early in the process cycle.

- The Capacitance Shunt Discharge principle produces a higher current in the anodize pore structure at a lower voltage and wattage.

- CSD (Capacitance Shunt Discharge) when used with Pulse Ramp during the first 5-10 minutes will always produce a faster harder anodize coating due to increased amperage and current density at lower voltages (Additional Data Logger Graphs Available.)

- Pulse Ramp, PSR, and CSD working together simplify all Manual and Automatic Running Procedures with a faster ramp to running current density.

- Low Sulfuric Mixed Electrolytes will produce quality Type II and Type III hard anodize dyed coatings in the same process tank at temperatures up to 100˚ F.

- Titanium Alloys used in Medical and Aerospace applications can be anodized successfully in Low Sulfuric Mixed Electrolytes.

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