Maximizing the Potential Future of Type II-III Anodizing Pushing the Envelope for Maximum Efficiency and Energy Savings

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A Practical New Age Production System for Type II and Type III Anodize (including Heavy Hard Salvage 5-10 mils) will be presented which covers the Complete Spectrum of Quality, Efficiency, and Energy Savings. Three critical areas will be discussed, the combination of which will raise the anodize process to new levels of excellence: (1) Simple modifications of existing chemistry accelerating anodizing rates over 100%, (2) Reductions in pulse – ramp – dwell times, increasing production with lower energy consumption, and (3) Special Sealing Solutions and Techniques providing corrosion resistance without sacrificing total hardness (abrasion resistance). Detailed data logger graphs from production facilities will be included.

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This paper presents a new age production anodize system which will potentially revolutionize the future of anodizing, while keeping up with the ever more demanding aerospace and in-service requirements. Using the data presented, the anodizer will be able to push the envelope, by maximizing efficiency and energy savings while using one process tank for both Type II and Type III anodize, which will meet and even exceed commercial, military, and high tech aerospace requirements. A new anodize test evaluation cell is introduced along with technical data so that the anodizer can evaluate process tank performance on a continuous basis. New sealing solutions and techniques are also revealed to establish final product quality as related to both hardness and corrosion resistance.

The paper which was presented at Sur Fin 2006 – "Complete Spectrum Guide to Top Quality Anodizing" – revealed and criticized ranges, parameters, and operating procedures for many commercial, military, and aircraft specifications. This year's paper will "zero in" on specific parameters, which will maximize the potential future of Type II and Type III anodizing while pushing the envelope with one universal process tank. Over the past year, there have been some significant improvements made using just one universal process tank, all relative to process time, efficiency, and energy savings, with final results exceeding 100% in many cases. One must consider it to be a savings exceeding 100% when there are very dramatic increases in efficiency as well as reductions in energy usage, along with a 50% reduction in process time.

When the information and data presented in each section of this paper are all applied together, the operator can really push that envelope for the maximum efficiency and energy savings necessary for future requirements as follows:

- I Process Tank Formulation and Specifications
- II Pulse Ramp Waveforms and Procedures
- III Anodic Sealing Formulations and Procedures
- IV Anodize Test Evaluation Control Cells
- V Electropolish/Activation Formulation/Procedure
- VI Special Present and Future Processes.
- VII Conclusions

I – PROCESS TANK FORMULATION AND SPECIFICATIONS:

One major purpose of this paper is to "zero in" on chemical ranges presented in our "Complete Spectrum Guide", and then further expand and really push the envelope with one universal range for both Type II and III anodize by introducing a special advanced, concentrated, universal or Multipurpose Additive Formulation designed as ACMAE (Activated Concentrated MAE).¹

There are a few basics which need review before presenting the chemical formulations and ranges so as to understand how chemistry affects the surface finish and anodize buildup. When evaluating dull and/or soft powdery coatings, there are various factors that are always related, when starting with a good microfinish or bright part and anodizing over an extended time period:

Good microfinish or bright parts eventually... Turn into a dull part (lost microfinish) over time... Which is the beginning of and leads to... Soft powdery coatings all due to... <u>Anodize Time – High Acid Conc. – Low Additive Conc. – Current Density</u> (Low or high current density depending upon temperature)

Over the years, this soft or potential powder situation has arisen countless times. The final analysis, evaluation, and answer as related to chemistry is to develop a better range or set of proven established parameters which will reduce loss of microfinish and maintain a hard bright finish. They can be summarized as follows:

With chemistry and other variable factors established... Good microfinish or bright part-pulse step ramped... 10 – (25-40) ASF within 6 – 12 minutes... With amperage decay 5 – 10% at constant CD... Maintaining a hard bright good microfinish with... Reduced Anodize Process Run Time and Pulsed Amp Hours

After extensive process review and production analysis over the years, the following operating ranges and/or parameters for the present and future processing of both Type II and III anodizing have been established. This anodize solution formulation along with the alternative types should be acceptable for processing to all present and most potential future requirements necessary for Hard Type II and Super Hard Type III on all aluminum alloys including 2024, 2011, 7075, and 7050.

Type II (Hard Type 23) and Super Hard Type III ACMAE –1 Type II (Hard Type 23)

Summer Actu (1166)10.3 ($11.0 - 14.0$) -13% VOI	
(<i>20.1 - 25.6</i>) % wt/vol	
Oxalic/Tartaric Acid1.0 – 3.0% wt/vol	
Additive (MAE)	
[Glycolic Acid + Glycerin - MAE (Multipurpose Anodize Electroly	$te)]^1$
Aluminum15.0 g/l max	
Temperature $35 - 75^{\circ}$ F	
Current Density	
Air Agitation	ace

ACMAE –2 Super Hard Type III-(23 SHC)

Sulfuric Acid (free)	.10.5 (11.0-14.0) -15% vol
	(20.1 - 25.6) % wt/vol
Add/Modifier (SP–ACMAE–2)	3.0 - 5.0% wt vol
(Presented at Sur Fin 2005 as	AHXMEP-5 Powder)
Aluminum	25.0 g/l max
Temperature	35 – 95° F
Current Density	20 – 75+ ASF
Air Agitation	3.0 - 5.0 cfm/sq ft of soln surface

The alternative ACMAE–2 is, in reality, a special concentrated MAE solution which is formulated using polycarboxylic acids.^{14.2} However; it is further activated and enhanced with aminopolycarboxylic acids^{2,3} which has an activating and electropolishing effect on the surface at the beginning of, and during the ramp cycle. The ACMAE–1 and ACMAE–2 additives can both be used for electropolishing as an excellent surface activator which will be presented later in the paper.

Far superior anodic coatings with excellent hardness while maintaining fine microfinish have been produced by replacing the sulfuric acid with organic carboxylic acids. These coatings also have much better dielectric properties. One particular formulation which has been used in production is as follows:

ACMAE – 3

Oxalic Acid	4.0 - 6.0% wt/vol
Tartaric Acid	5.0 – 8.0% wt/vol
Additive (MAE)	5.0 – 10% vol
Temperature	50-75° F
Current Density	10 – 35 ASF
Agitation	Eductors (soln pumped)

This process solution will produce coatings up to 2.5 mils with excellent hardness. However, the voltage requirements are much higher (70–100 volts for 2.0 mils). The hardness and microfinish of thin coatings (0.5–1.5 mils) produced in organic acid electrolytes are far superior to those produced in sulfuric acid, making them important in certain specific electronic applications.

Note:

One important area which needs to be discussed is the testing of these electrolytes along with continuous analysis, evaluation, and maintenance of production tanks, using a unique test evaluation cell which will be presented in section IV.

II – PULSE RAMP WAVEFORMS AND PROCEDURES

Now that the proper tank chemistry and operating ranges have been established, the next step is to present the best possible ramp and run procedures necessary to meet present and future potential process requirements. Again, one must "zero in" on the best pulse ramp specifications along with actual pulse-step-ramp procedures proven in production.

The requirements for the basic rectifiers, rectifier pulse, and external pulse units must be reviewed before presenting actual procedures. Rectifiers should be full wave secondary SCR or half wave secondary SCR for faster anodize buildup and activation of anodize chemistry. Preferred rectifiers are secondary SCR center tap (that is center tapped transformer) for better efficiency due to the higher SCR pulse at low voltages. This can be summarized with voltage requirements including CSD* for Type II and III anodize as follows:

Type II Anodize (including Type 23 – 2.0 mils in 30 – 50 min) 30 Volts Full Wave secondary SCR center tap with CSD Type III Anodize (including Type 23 – 2.0 mils in 20 – 30 min) 75 Volts Full Wave secondary SCR center tap with CSD 75 Volts Half Wave secondary SCR center tap with CSD *(CSD refers to Capacitance Shunt Discharge)^{4,7,8}

There are many different pulse units in-service which operate at low and high frequency using various time cycles. This has been researched for over 40 years in diversified production areas with many qualified anodize personnel. Over the past 10 years there has been considerable production testing done to confirm the importance of low frequency pulse, due to the fact that it takes advantage of recovery time.^{5,6,14,1} The ranges are wide open due to various alloys and high tech requirements. However, this paper presents specific specifications which will work on most alloys used in production, both today and for the foreseeable future. They are as follows:

Pulse Time Cycle/Duration
HP – High Pulse On Time $0.5 - (1.0 - 2.0) - 4.0$ sec
Off Time $0.5 - (1.0 - 2.0) - 4.0$ sec
HP – Current10 – 25% above operating current
LP – Low Pulse On Time $0.5 - (2.0) - 4.0$ sec
Off TimeTotal HP Time Cycle
LP – Current
PSR – Pulse Step Ramp/Dwell
PSR Run (On Time)) $(0.5 - 1.0) - 5.0 \text{ min}$
PSR Dwell (Off Time) $(0.5 - 1.0) - 5.0 \text{ min}$

Now, proper pulse ramp procedure must be reviewed. Please note this is one of the most important sections of this paper. The anodizer must realize that the first 5 - 10 minutes of the anodize run are critical as related to Final Quality, Efficiency, and Energy Savings. During this ramp time, a good and proper pore structure must be developed and maintained. There are three very important reasons for this:

- 1. Faster and Heavier Anodize Buildup
 - (Reduced Anodize Time Increased Efficiency)
- 2. Better Faster Dye Penetration
- 3. Better Final Seal Capability

There are four specific variable control factors that must be incorporated into the pulse ramp procedures if we are to really push that envelope with the process capability to maximize efficiency on present day as well as potential future anodizing. They can be summarized as follows:

- 1. Use Pulse Step Ramp together
- 2. Ramp Time to constant current density
- 3. Ampere Decay (ADO) at constant current density
- Use CSD if available per specs noted in ref: Sur Fin 2003 paper pg 82⁶

Over the years, many procedures have been established for specific alloys. Specialized procedures can be worked out to meet specific requirements. Included herein are proven procedures to be used as basic examples. They have been proven to produce quality anodize while maximizing present and potential future efficiency and energy savings.

Numerous successful ramp procedures have been reviewed which were developed for various alloys, specific part assemblies, and in-service requirements. The following basic data logger Pulse-Step-Ramp graphs made during heavy production, not including full running constant current density (RCCD) detail, are included as informational examples:



STANDARD RAMP – 10 MIN PULSE – STEP – RAMP 10 Min Pulse 222H2L – R12D1 (2 Sec. Pulse / 1 Min Dwell periods) Hard Anodize (6061) 2.0 Mils – 30 Min (35 – 45 ASF) Sulfuric Type II (23 Hard) 0.2 – 0.5 Mils – 12 Min (20 – 25 ASF)



STANDARD SHORT RAMP – 5 MIN LOW PULSE - STEP - RAMP 5 Min Low Pulse (0.5 Min Run – 1.0 Min Dwell – 1.4 V/Min) Hard Anodize (7075) 3.0 Mils – 40 Min (40 – 45 ASF)



STANDARD LONG RAMP – 15 MIN PULSE – STEP – RAMP 15 Min High Pulse (0.5Min Run – 1.0 Min Dwell – 0.7V/Min) Hard Anodize (2024) 2.0 Mils – 35 Min (40 ASF) Sulfuric Type II (23) Dyed BK (0.5 – 0.8 Mil) 25 Min -25 ASF



AIRCRAFT JET ENGINE PARTS Manual Run – 750 Amps (Auto PSR – 1375 Amps) 40 ASF (10% Decay) \rightarrow 25 Min (High Pulse) \rightarrow 33Min



LOW VOLTAGE PULSE + CSD (Capacitance Shunt Discharge) 5 – 10 % High Current Pulse + CSD (Needed for Basic Electrochemical Activation)



LOW / HIGH VOLTAGE PULSE + CSD 15 – 20 % High Current Pulse + CSD CSD in Operation Maintains High Current



5 MIN PULSE STEP RAMP HIGH VOLTAGE (20 – 25 % HIGH CURRENT) PULSE + CSD Type II (23 Hard) Clear Anodize 0.3 -0.7 Mil (20 -25 ASF) - 80°F Hard Anodize Flash 0.4 – 0.8 Mil (35 – 40 ASF) - 45°F



10 MIN PULSE STEP RAMP HIGH VOLTAGE (20 – 25 % HIGH CURRENT) PULSE + CSD Production Standard (20 – 25 % High Current Developed Later in Run) Note High Pulsed Current maintained at RCCD

III – ANODIC SEALING FORMULATIONS AND PROCEDURES

In many cases, <u>both</u> hardness and corrosion resistance are important factors for final in-service requirements. This has always been a problem because there normally must be some degree of loss in hardness during the sealing process. In the past a "boiling" 5% sodium dichromate seal¹⁰ was used on hard anodize when hardness was the <u>real</u> priority. This 5% sodium dichromate (10 – 15 min seal or longer), which is still being used, is a real killer when it comes to the final hardness of the coating. I was actually instrumental in having the dichromate seal removed from Mil – A – 8625 <u>C</u>. Since then hard anodize is not to be sealed when hardness is the main objective unless called out by the customer and/or contracting agency procurement documents. When corrosion resistance along with good hardness <u>is</u> a requirement, special sealing techniques must be utilized.

This section will review various sealing solution formulations and procedures which are effective without sacrificing major hardness characteristics. Using these formulations, anodic coatings should pass hardness (taber abrasion) tests, in addition to most corrosion resistance (salt spray) tests. Examples of these are two standard low temperature seals, manufactured by <u>Major Suppliers to the anodize industry</u>, designated as MJSP with no reference to the actual supplier. Also included are several different seals listed a LTCS (low temp cold seals) and RL/HTS (reduced low/high temp seals). They are as follows:

LTCS #1 Low Temp Seal – (MJSP #1S)

Conc	1.8 – 2.2% vol
Nickel Metal	0.90 – 1.1 g/l
Fluoride	500 – 650+ ppm
Temp	
pH	5.8 – 6.1+
Immersion Time	5 – 10 min

LTCS #2 Low Temp Seal – (MJSP #2S)

Conc	1.5 – 2.5% vol
Temp	$\dots 80 - 90^{\circ} F$
pH	5.5 – 6.5
İmmersion Time	5 – 10 min

Triethanolamine ^{14.3}	0.5 - 1.5%
Fluoride	500 – 1000 ppm
Temp	$\dots .75 - 140^{\circ} \text{ F}^{11}$
pH	6.5 – 8.0
Immersion Time	$0.5 - 2 \min$

RL/HTS #4 Nickel Acetate/Fluoride Seal (MJSP #4)

Conc	1.0 – 2.5 oz/gal (MJSP)
Fluoride	Per MJSP
Temp	150 – 185° F
рН	5.5 – 6.5
Silicates	10 PPM max
Immersion Time	3 – 8 min

RL/HTS #5 Dilute Chromate Seal¹² (use in Duplex Seal) Potassium Chromate.....0.03 – 0.06% wt/vol Temp......145 – 160° F pH......3.2 – 4.5 Silicates......10 PPM max Immersion Time......1 – 5 min

RL/HTS #6 Sodium Dichromate Seal^{12,13} (use in Duplex Seal) Sodium Dichromate......0.5 – 1.0% wt/vol Temp......145 – 160° F pH......5.0 – 6.5 Immersion Time......1 – 3 min

RL/HTS #7 Teflon /Fluoride Activator/Seal¹²

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Anodic Seal Procedures:

Several different seal procedures have been investigated and used in limited production as related to both hardness and corrosion resistance. Two basic seal procedures are as follows:

Low Temp Seal Procedure – LTCS

Procedure directly after anodize tap water rinse

- 1. DI Water Rinse
- 2. Seal / Activator LTCS #3 (one minute)
- 3. DI Water Rinse
- 4. Seal in LTCS #1 or #2 (5 min)
- 5. DI Water Rinse
- 6. Seal / Activator LTCS #3 $(1 2 \min)$
- 7. DI Water Rinse
- 8. Dilute Chromate Seal RL/HTS #5 (1 2 min)
- 9. DI Water Rinse

Reduced Low/High Temp Seal Procedure - RL/HTS

- Procedure directly after anodize tap water rinse
 - 1. DI Water Rinse
 - 2. Seal / Activator LTCS #3 (one minute)
 - 3. DI Water Rinse
 - 4. Seal in RL/HTS #4 (3 5 min)
 - 5. DI Water Rinse
 - 6. Seal / Activator LTCS #3 $(1 2 \min)$
 - 7. DI Water Rinse
 - 8. Sodium Dichromate Seal RL/HTS #6 (one minute)
 - 9. DI Water Rinse

IV – ANODIZE TEST EVALUATION CONTROL CELLS:

The Hull Cell and many other small test cells have been used for the control of Plating Solutions. However, very few test cells have been developed specifically for Anodizing with limited published data available.

There have been four basic cell types which I have used for the development, evaluation, and control of anodize solutions. These cells have become very important in seven particular areas as follows:

- 1. Anodizing Specific Alloys: Checking the Capability to run Alloys that burn easily (2011, 2219, and 7050).
- 2. Ramp and Running Procedures: Checking Running Procedures to control and eliminate smut + dull coating.
- 3. Hardness: Running test panels to establish the best procedure for maximum hardness.
- 4. Additives Modifiers: Test Cell represents the best control as relative to concentration, efficiency, and <u>Throwing Power</u> (TP).
- 5. Solution Performance: Easier evaluation at higher temperatures using 5 gallon sample.
- 6. Salvage: Anodizing small parts producing 10 20 Mils using Auxiliary Cathodes.
- 7. Pushing the Envelope for the potential capability of present and future processing with solution modifications.

Presented here is one of the many cells which have been used for the research, development, evaluation, and control of Anodize process tanks and systems, designated as the ADEC Cell.

Additional design and operating parameters are available upon request.



POLYCARBONATE (LEXAN) CELL: 5 LITER CAPACITY Dimensions: 6" X 6" X 12" Deep.... Submersible Pumping: 5 – 10 Liters / Min Anode: 2 – 4" X 4" Test Panels Current Density Operating Range: 10 – 100 ASF

V – ELECTROPOLISH/ACTIVATION - FORMULATION/PROCEDURE

The electropolish process can serve as an excellent cleaner and activator for the Anodizing process. This process operates on a molecular level and can be, in many cases, the best guarantee for a really clean active surface. Even during earlier years in anodizing, when processing prototype and/or critical parts for the F-18 Hornet, electropolish activation was used as a precaution for all 7000 series aluminum just prior to anodize. Here are four particular areas where electropolishing can be very beneficial to the anodize process.

- 1. Superior cleaning prior to anodize
- 2. Superior activation (30 60 sec) leading to faster anodize buildup and better quality
- 3. Bright Finish replacing Bright Dip (no heavy fumes)
- 4. Deburring of sharp edges

Electropolishing of aluminum can be done at room temperature <u>without</u> the heavy hazardous fumes from phosphoric Nitric Bright Dips. Included here is one particular formulation for electropolish on aluminum which actually includes the MAE additive in a simplified basic make up.

Phosphoric Acid	80 – 95% vol
STD MAE Additive	5.0 – 20% vol
Temperature	70 – 110° F
Current Density	75 – 150 ASF
Time	$0.5 - 5.0 \min$
Heavy Mechanical or Pumped Agitation	

Electropolishing time can vary from 30 sec to 5 min depending upon activation and/or final surface finish requirements, including material loss and dimensional considerations.

The incorporation of electropolish into the anodize process will – no doubt – be another important part of the potential future of Type II and III anodizing as related to maximum efficiency and energy savings.

VI – SPECIAL PRESENT AND FUTURE PROCESSES

Only limited basic data regarding present research and development in three specific production areas can be presented here. Some anodizing facilities are using the following information on specialized parts that have been in service.

Salvage Heavy Thickness Anodize:

Heavy Thickness Hard Anodize (5 - 10 mils) is being produced in production using Half Wave Secondary SCR Rectifiers very successfully. We really "zero in" on a narrow process solution formulation for this application.

Sulfuric Acid (free)	.10.5 – 12.0% vol
Modifier (SP – ACMAE – 2)	.5.0 – 7.0% wt/vol
Aluminum	.10.0 g/l max
Temperature	$35 - 60^{\circ} \text{ F}$
Current Density	.20 – 35 ASF
Air Agitation	3.0 - 5.0 CFM/ Sq Ft Soln Surface

Electrocolor:

There have been several requests for the development of a hard bright electrocolor process. Successful production has been carried out using these two production stages:

- 1. 20 min Anodize Ramp to 40 45 ASF at 85° F
- 2. Modified Cobalt Electrocolor System with 5 8 min Ramp.

Using this system hard black electrocolor coatings were produced maintaining good brightness and microfinish. Silver white to white electrocolor coatings have also been produced with extreme hardness.

Multi–System Sealing:

Development work is being carried out with limited production on a Multi-System Seal which incorporates Teflon, Cobalt, and Fluoride in one seal tank along with Pulse AC and / or DC current. This system designated COTEF has been limited to special high tech applications at the present time, but could have a significant impact on the future of anodizing.

VII – SUMMARY / CONCLUSIONS:

- 1. When the process tank chemistry and Pulse–Step–Ramp procedures presented in this paper are applied and used as a complete package, efficiency and energy savings will exceed 100% over Standard Type II and III Anodizing.
- 2. The specific process tank chemical formulations presented can be used for both Type II and III Anodize, reducing process time 50% or more.
- 3. Type II and III Anodize can be performed in one universal process tank meeting and exceeding all applicable specifications.
- 4. When specific (2 Sec) Pulse-Step-Ramp waveform parameters and dwell procedures are used together with Amperage Decay <u>then</u> efficiency and energy savings can be increased by 25-50%.
- 5. All alloys can be processed in the same electrolyte for both Type II and III Anodizing, when additives and modifiers are maintained at higher concentrations.

Higher Acid Concentrations are no longer necessary for 2000 series.

Good quality hard coating on 7000 series with concentrated MAE (5-10%).

- 6. The Lower Temperature Reduced Time Seals presented here will increase corrosion resistance without a major loss of hardness.
- 7. Incorporating Electropolish into the Anodize Process can be an excellent Cleaner and Activator just prior to the Anodize Ramp Cycle.
- 8. The Anodize Development Evaluation Control (ADEC) Cell can be very useful for process tank control when pushing the envelope for maximum coating buildup and Throwing Power (TP).
- 9. By expanding upon today's technology using evaluation tools such as the ADEC, the future of anodizing should have endless possibilities for improvement by pushing the envelope for maximum efficiency and energy savings.

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