Anodize Additives and Pulse Ramp Systems
Optimizing the Chemistry and the Power

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The basic additives and pulse ramp systems available to the anodizer will be discussed in relation to their functions and operations in the anodize process. We will try to answer the question *"How can the reactions and procedures really work to produce a better quality anodic coating in a shorter time with more efficient use of electrical energy?"* Graphic data, including a new additive pulse ramp development, will be presented, covering hardness (wear), temp, amp-hours, voltage and time with comparative analyses. Data submitted will cover production work in the commercial aircraft/aerospace and military areas over the past 43 years.

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ANODIZE ADDITIVES AND PULSE RAMP SYSTEMS OPTIMIZING THE CHEMISTRY AND THE POWER

The major content of this paper is to present information relative to the functions and operations of anodize additives and pulse ramp systems in the anodize process. I feel this is important because a considerable amount of basic information has not been made available or properly presented to anodize owners, managers, and operators. I also feel that it is my personal commitment to make this data available to the anodize industry relative to the advantages of all available systems. In addition, the pulse ramp systems do work together with anodize additives producing electrochemical reactions optimizing the chemistry and the power.

I have worked with various chemical additives and electrical pulse ramp systems used in anodizing since 1960. There have been special research projects along with heavy production on both military and commercial work. I find that there have been misunderstandings as to how these additives actually work or function. The available literature has been in error or incomplete. I will present data on how these additives and pulse ramp systems function to produce higher quality anodize coatings. In addition, a new unique electrochemical pulse ramp development will be presented which has been tested in production up to 6000 amps with excellent results.

Improvements, advantages, and new developments will be noted by dividing the data into five areas as follows:

I. How chemical additives function in the anodize tank
II. How pulse and pulse ramp function in the anodize process
III. How chemical additives and pulse ramp systems work together
IV. How a new capacitance inductance shunt discharge system improves the electrochemical pulse ramp cycle
V. Graphic Comparison: Additives-Pulse Ramp-Related Control Factors

I. ANODIZE ADDITIVES: FUNCTIONS

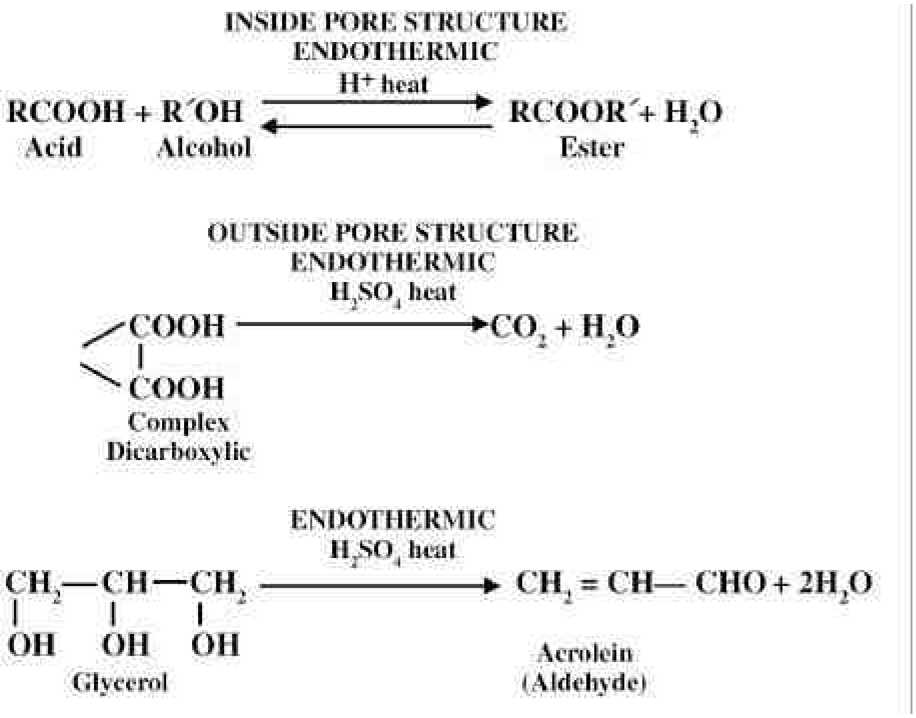
I have reviewed 5 major anodize chemical additives supplied to the anodize industry. These additives supplied by 5 different companies all contain one or more of the following types of chemicals:

- CARBOXYLIC ACIDS – ALCOA ALUMILITE
- ALCOHOLS – REYNOLDS MAE[1-2]
- LIGNIN PRODUCTS (SULFONATES)[3-7]
- METAL COMPLEXING AGENTS[8-9]

Anodize additives enter into various chemical reactions which result in harder coatings and faster deposition rates. This results in lower electrical energy used due to reduced amp hours and lower final voltages at the end of the anodize process run. Some of the more important chemical reactions and results will be presented at this time.

Excess heat and resistance develops in the anodize pore area due to wattage (W = Volts x Amps) related to the anodic electrochemical reactions, which occur during the formation of aluminum oxide. This excess heat in the pore structure area is removed through endothermic additive reactions on a molecular basis. The catalyst for the endothermic reactions is hot sulfuric acid, which will soften the coating over a period of time. These endothermic reactions absorb the hot acid reducing the dissolution of the anodic film, thereby producing a harder coating. I have referenced only Alcoa Alumilite and Reynolds MAE because they represent the basic pioneers in this area. There have been other additives developed which use some of this basic chemistry with more efficiency at different energy levels in certain high tech and heavy production areas.[6-9]

Some examples of these endothermic reactions are noted below. You will notice one takes advantage of a reversible equilibrium.



The various additives available utilize these endothermic reaction principles to different degrees in somewhat similar reaction methods and/or mechanisms. The degree of efficiency for these Endothermic Reactions on a Molecular Basis makes it possible to anodize at much higher temperatures. Standard Type II sulfuric and hard anodize have been processed at temperatures starting at 40°F up to as high as 110°F in some cases. You may ask – ***Why the high temperature?*** Three points are evident.

1. Dye Capability (Lighter Coatings)
2. Micro finish
3. Power Savings (Refrigeration)

Anodize additives also activate the aluminum alloy surface to be anodized by complex ion activity in certain cases. It has been noted that specific alloys (2000 series) such as 2024, 2011, 2219 form basic, more uniform anodic coatings with reduced or no burning problems early in the process run.

Data is available on how these complexes form and exist to a limited degree due to polar bonds and equilibrium shift. Examples of these complex ions are indicated in figures below.

These metal complex systems have been added to improve the uniformity and final hardness of anodic coatings produced on 2000 and 7000 series alloys meeting and/or exceeding military specifications.

Anodize additives have a direct effect on pore structure. This is an area that has been missed or overlooked by many anodizers. The pore structure could be formed or developed more efficiently to meet specific requirements. The evolution of heat and gaseous products is actually controlled by the anodize additive concentration as related to acid concentration, air/CO agitation and temperatures as high as 120°F.

Please note at this point – this pore structure development, through additive chemistry, also uses lower amperage current densities more efficiently for the production of the final anodic coating.

The pore structure development is finally directly related to maintaining a better micro-finish with increased dye penetration resulting in brighter, more attractive dye colors and harder final finishes.

Different types of ramp and pulse ramp systems with dwell have been found to work together with additives to control, develop, and/or produce specific desirable pore structures on all the aluminum alloy types (1000 – 7000 series) including die cast such as 380.

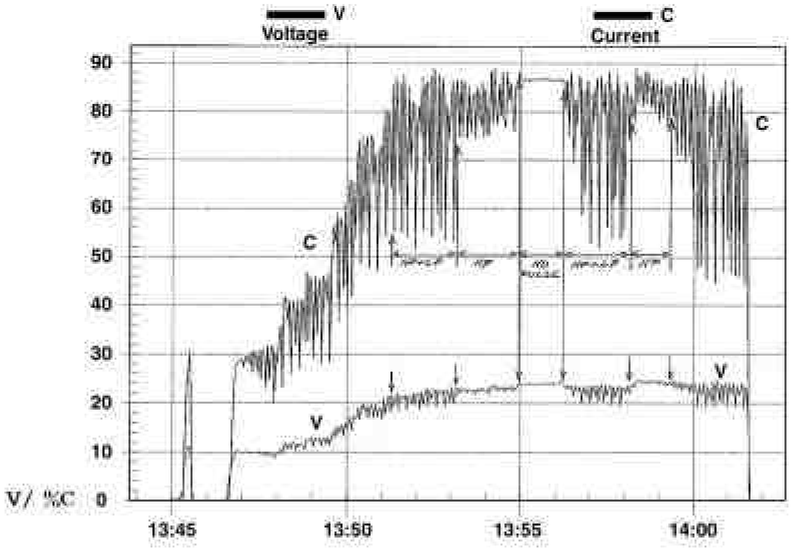
Now—you see we have bridged the gap where electrical pulse systems support and improve chemical additive reactions through the pore structure.

II. PULSE/PULSE RAMP SYSTEMS

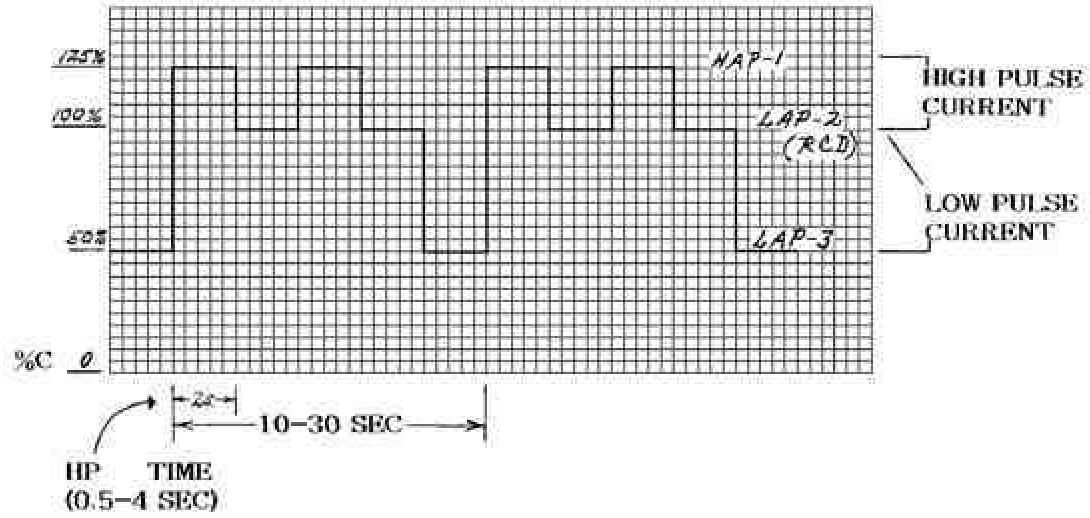
We have studied various pulse systems available to the anodizer. There have been AC/DC generators superimposed back as far as 1957 leading to 400 cycles and the present High Frequency Pulse Systems. One thing is certain – High Frequency Pulse is not the answer in many cases as people have been misled to believe.

Many pulse rectifiers utilize a variable low to high frequency pulse which allows the use of higher current densities to speed up the anodize process. There is also a reduction in the tendency to burn certain aluminum alloys such as 2024-2011 due to the pulse ramp principle. Try to remember the higher frequencies become less effective in certain cases. ***Also – why not try to utilize lower current densities more efficiently?***

Various slow (very low frequency square wave) high and low pulse systems have been developed which take advantage of the recovery effect with recorded success.[10] These systems have been overlooked and/or underestimated because they have been, for the most part, a matter of proprietary technique. However, when they are used in various pulse time modes from 0.5 – 10 – 30 seconds, the results can be quite favorable. If the slow high and low pulse systems are used along with standard pulse rectifiers, even more favorable results can be achieved. The coatings are produced harder and faster. Please note at this time – the chemical additive efficiency is also improved due to relaxation time in the pore structure during the slow low pulse cycle. Two examples of the slow high and low pulse systems are noted below.



HIGH PULSE HP TIME: 0.5-3 SEC HP CURRENT: 100-125%
LOW PULSE LP TIME: 2-10 SEC LP CURRENT: 100-50%



The slow high and low pulse systems have also been used on various half-wave rectifiers. Many reports of quality hard anodize coatings with reduced process times have been made over the past few years. Some of these half-wave, three phase rectifiers have a built in 22% ripple with as much as 40% at lower voltages. This results in a built in 60-cycle pulse, which produces excellent results when used with the slow high and low pulse systems.

III. ANODIZE ADDITIVES – PULSE RAMP SYSTEMS – WORKING TOGETHER

Anodize additives and pulse ramp systems reduce heat energy in the pore structure through different reactions and methods. However, there are some reactions where efficiency is shared to some degree on a timeshare basis. Therefore, chemical additives and pulse ramp systems should be used together, whether the reactions are independent or timeshared. The maximum process efficiency is a reality when both are used together in the same tank at the same time. Please consider the following factors, which have been found to operate together on a timeshare basis with considerable advantage at certain anodize facilities.

A. Relaxation Time ---Current vs. Additive Reaction rates within pore structure
B. Recovery Effect ----Chemical Reaction Activation
C. Pulse Ramp Rate --Chemical additive concentration
Polarity Equilibrium Shift

A. Relaxation Time – DC Current vs. Additive Reaction Rates

The relaxation time represents one area where the low pulse DC current and chemical additive reactions timeshare the energy and heat reduction in the pore structure of the anodic coating simultaneously. The acceleration and degree of this energy reduction is dependent upon total DC current drop and time duration during the low pulse cycle. The low pulse reduces gassing and ionic activity in the pore structure allowing other additive reactions to accelerate more efficiently with some consideration given to polar complex ions. The polar ions do increase electrochemical activity. There has been data referred to me with reference to the functions of Lignin Sulfonate additives in this area.

We have already noted that the pore structure is developed and can be controlled to some degree during the low pulse cycle and relaxation time. Therefore, this time period should be taken into consideration when processing parts that are going to be dyed requiring a good pore structure.

B. Recovery Effect: Chemical additive reaction activation – Electrochemical Pulse

The recovery effect has been investigated by various research people and found to be very important to the anodize process.[10] During this recovery effect, the applied current will reach a new value higher than that value noted just before the low pulse began its fast decrease. This current surge forward at the end of each low pulse cycle utilizes the recovery effect in many areas.

1. Ionic endothermic reactions accelerate before peak gassing occurs.

2. Endothermic additive reactions occur at lower energy levels (promoting improved micro-finish – brighter dye finishes).

3. All ionic reactions are immediately accelerated forward with the development of a higher current density non-existent just before the low pulse cycle.

We find the recovery effect to be very important in all types of pulse. Remember, when it is really happening, the additive chemistry is at a point where it must/should and can function more efficiently. There are numerous graphs relating this to production parts available upon request. They all relate to the following end results.

1. Harder coating

2. Improved pore structure (dye absorption/sealing)

3. Faster anodic coating formation rate

C. Pulse Ramp Rate – Chemical Additive Concentration Polarity – Equilibrium Shift

The pulse ramp rate and chemical additive concentration do increase efficiency in the anodize process to a greater degree when operating together. Many additives have been evaluated in this area. The additive concentration usually has to be near its maximum for best results due to the polarity of the ions and/or complex ions depending upon the carboxylic acid alcohol arrangement in the particular anodize chemical additive.

I found the pulse ramp rate would give more favorable results between 100-15 CPM (Cycles Per Minute) on various alloys. This corresponds to a pulse (on/off) time of 0.5 – 2.0 seconds per pulse. In each case the additive concentrations were more effective at their higher recommended concentrations.

Tests have been conducted to verify efficiency as related to the total current and time used for the production of 1-2 mil anodic coatings. One fact was established which can be easily verified. Various alloys formed their first 0.5 – 1.0 mil anodic coating faster with the same ASF applied in each case. I also found data indicating lower ampere-hour usage. This is an indication that more electrons (amp hours) are being consumed for the production of anodize rather than gaseous byproducts.

The tests indicate the highest efficiency only when pulse ramp time was integrated with high additive concentrations. This shifted the equilibrium to utilize more available electrons for the production of anodize. This can be verified to some degree by simply monitoring (watching) 2000 series (2024/2011) being ramped from 10 to 20 Volts. The amperage consumed at the same ASF is considerably higher in specific cases. This higher amperage consumption produced more anodic coating with reduced time indicating greater efficiency.

IV. CAPACITANCE SHUNT DISCHARGE – IMPROVING THE ELECTROCHEMICAL PULSE RAMP CYCLE

At this time we would like to present a new type of capacitance shunt discharge system and show how it can make a remarkable improvement in the pulse ramp cycle. This also affects the chemical additive efficiency to such a degree that we must relate it to improving the electrochemical pulse ramp cycle.

BACKGROUND:

The capacitance developed between the anodize electrodes (anode // cathode) has been studied by various research groups as related to its opposition to the flow of pulsed current. This impedance factor results in higher voltages and heat developed in the pore structure during anodic coating build up. If we discharge this capacitance, the voltage is lowered, the amperage is increased and there is less heat to be removed by the additive endothermic reactions. The additive polar ions are being pulse activated at the anode while all these reactions are taking place.

This capacitance reactance (impedance) condition is very pronounced when half wave pulsed rectification is use in the anodize process during the beginning and early into the pulse ramp cycle leading to the running constant current density. The reader will see when this capacitance is discharged in a particular way; the result is much higher current densities at 20 – 45% lower voltages.

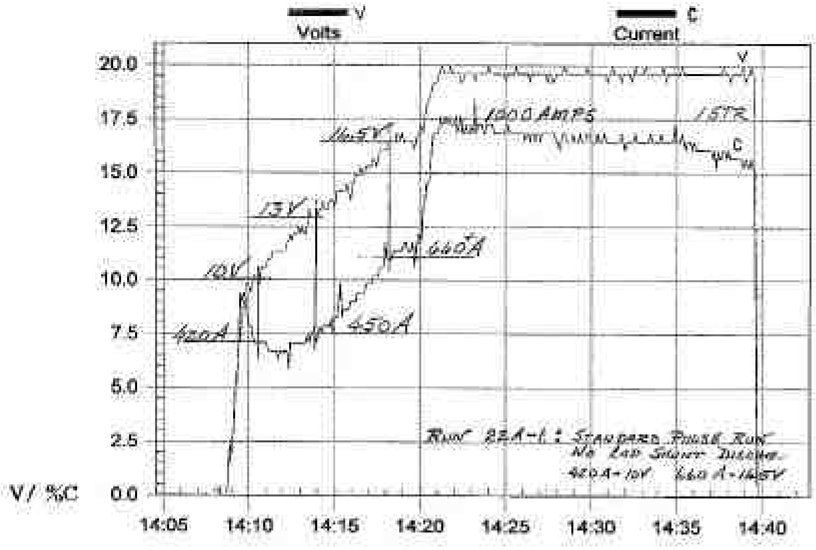
One particular patent refers to the use of a shunt discharge system, which increases the current density at a preset voltage by as much as 50%. However, this is only applicable to single phase half wave systems where the SCR must both rectify and control in the secondary of the transformer circuit.[11] The system is expensive and therefore not cost effective on high amperage loads. After three years of experimentation on production anodize lines, we have been able to perfect the capacitance discharge system on all half wave three phase anodize rectifier power supplies up to 100 Volts and 6000 Amps. Full wave systems have also been successful to a considerable degree. Examples are as follows:

Hard Anodize------------------100 Volts, 3000 Amps – Type III operated at 40-55° F

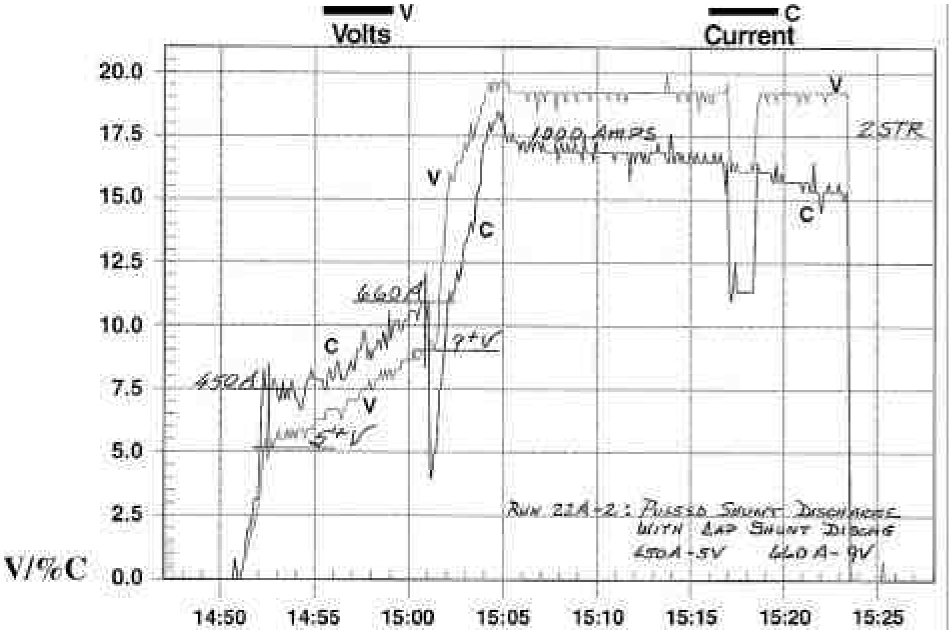
STD Anodize Type II –----- 15 Volts, 6000 Amps – 90 KVA
30 Volts, 6000 Amps – 180 KVA
Type II and Type III Anodize
Produced at 60 – 85 – 100 – 120° F

The system operates by pulse discharging capacitance developed during the anodize ramp cycle using special low resistance high wattage resistors. The rectifiers I used have quite high outputs up to 300 KVA. Therefore, I had to use a series/parallel resistance bank with a wattage capacity up to 12,000 watts at 20 Volts. These electrical pulse discharge requirements and parameters will be discussed in more detail later.

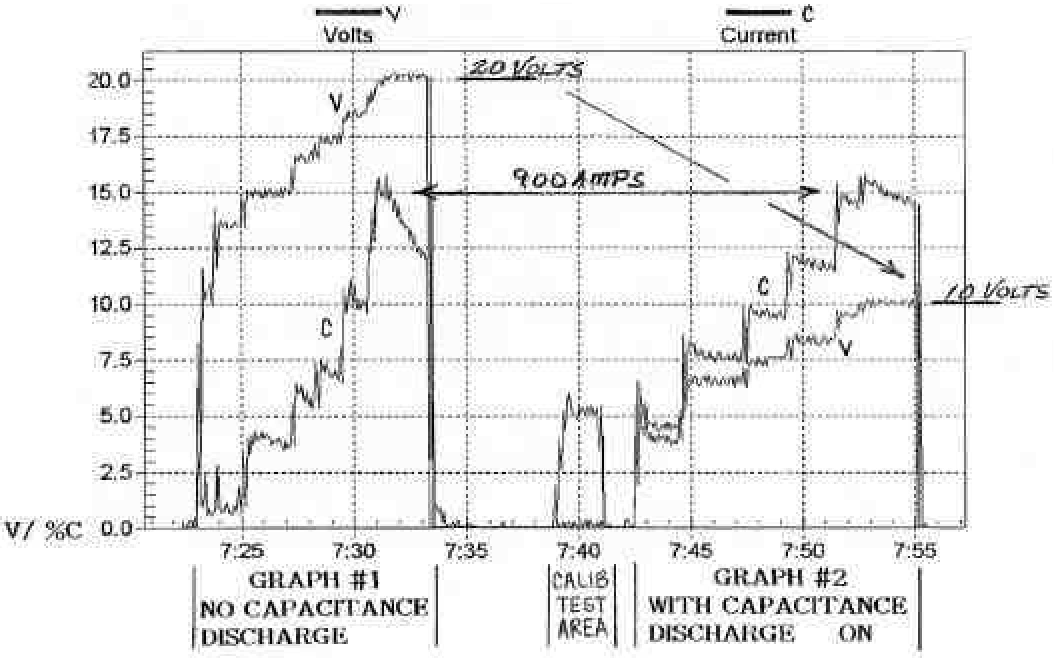
The following graphs were made with a data acquisition logger and laptop computer. They represent general process runs comparing results before and after the capacitance shunt discharge unit was connected to the process tank with a 30 Volt 6000 Amp half- wave rectifier. The load size was the same in both cases (50 sq. ft.). The load was ramped to 17.5% of 6000 or 1050 Amps. The final voltages were 19.5 and 19.0 respectfully.



The first run 22A-1 was made with a standard slow (low frequency square wave) pulse systems (LF/HP/LP) turned low. No capacitance shunt discharge unit was used on this run. The reader will see that we reach 420 Amps at 10V and 660 Amps at 16.5 Volts. The current appears to lag behind from 14:10 to 14:20. Finally, we reached 1000 amps at approximately 19.5 Volts. Please note for clarification, the X-axis of the graph represents both voltage and % total current output of rectifier. For example – in this case 17.5 represent 17.5 V and 17.5% of a 6000 Amp rectifier or 1050 which is indicated on graph as 1000 Amps. This V/ %C will be used on all graphs due to the data logger operations with graphic overlay.



The second run 22A-2 was made with the same pulse system (LF/HP/LP) turned low. The capacitance shunt discharge unit was connected to the rectifier and allowed to shunt approximately 10-15% current density during the entire run. A dramatic difference was noted at this time. Please note – we reach 450 Amps at 5 Volts and 660 Amps at 9V. The total heat generated from electrical energy during the pulse ramp was reduced by approximately 50% due to the reduced voltage during the first ten minutes or initial anodic coating formation. The pulse ramp was only on approximately 50% of the time allowing the anodize additive endothermic reactions to function more efficiently. This does represent a general type II sulfuric anodize ramp reproducible in most cases. Therefore, the energy reduction in the anodize pore structure will be approximately 50% during this pulse ramp cycle.



The next two graphs represent a capacitance shunt discharge system set up for maximum efficiency anodizing 2000 Series alloys such as 2024, 2011, 2219. The total current is represented as 15% of 6000 amps or 900 amps in both cases. Graph #1 represents a standard pulse ramp to 20 Volts reaching 900 amps at the end of the cycle with no capacitance shunt discharge connection. Please note – the voltage in graph #2 using the cap shunt discharge was only 10V at the end of the pulse ramp cycle. This 50% reduction in heat generation at only 10 Volts after reaching 40 ASF (900 amps) represents a valuable improvement for the production of superior hard anodize on 2000 series alloys with energy time savings and practically no chance of burning.

The advantages of using this system along with chemical additive chemistry are obvious from the preceding graphs.

At this time we will note the basic requirements for the successful operations of the capacitance shunt discharge system (CAP/SHT/DISCHG). The CAP/SHT/DISCHG current should never exceed 20% of the total anodize current for more than 0.5 sec during each pulse cycle. Please check the basic parameters and requirements used during the processing involved in the preceding graph. This will represent all systems depending on total current consumption as noted below.

PULSE CAP/SHT/DISCHG Time Range ………..100 – 15 CPM
HP Current (On Time)…………………………….0.5 – 2 SEC

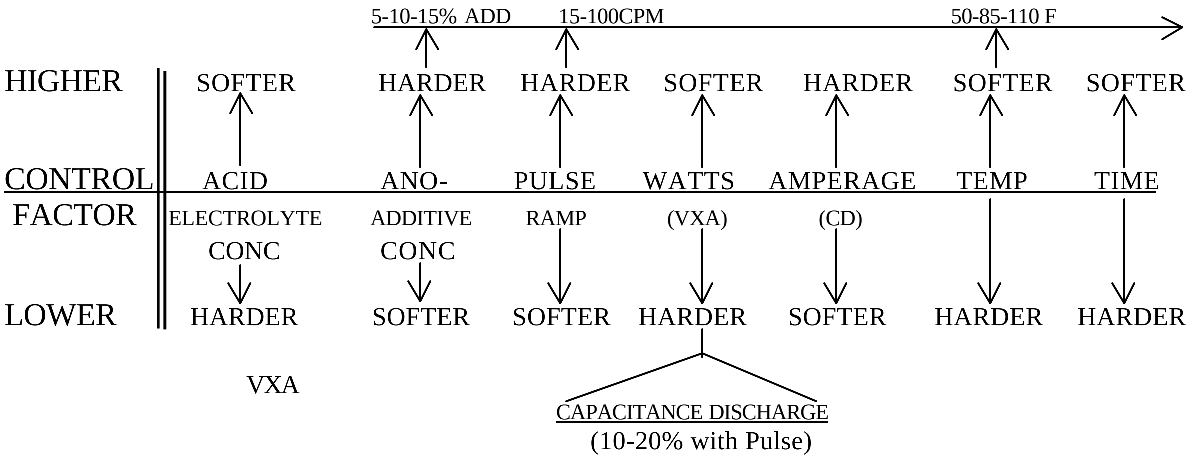
PULSE RESISTANCE SPECIFICATIONS: 1000/6000 Amps
1000 Amps: Shunt Discharge 200 Amps (20%)
Pulse Discharge Ramp to 20 Volts
200 Amps @ 20 V = 4000 Watts (0.1 OHM)
(Parallel 10 x 1.0 OHM Resistors)
(4000 Watt Resistance Bank)

6000 Amps: Shunt Discharge 600 Amps (10%)
Pulse Discharge Ramp to 10 Volts
600 Amps @ 10 V = 6000 Watts (0.0167 OHM)
(Parallel 10 x 0.167 OHM Resistors)
(6000 Watt Resistance Bank)

V. GRAPHIC COMPARISON: ADDITIVES-PULSE RAMP-RELATED CONTROL FACTOR

Several years ago I prepared a particular graphic chart which I use in training seminars to indicate how various control factors affect the quality of the anodize coatings as related to hardness or the formation of a soft powdery coating. This chart has been modified here to include pulse ramp rate and the capacitance shunt discharge as related to reduced voltage and wattage.

Check out this chart carefully for different process results depending upon which factor can be raised or lowered at your process facility.



We have stated and verified that the anodize process tank can be operated at temperatures up to 85-100°F on a production basis.

The chart has approximate ranges of operation dependent upon the type of pulse and particular chemical additive being used. The reader should note the additive concentration range (5-15%) is quite wide dependent upon the particular additive product from the supplier.

CONCLUSIONS

- Anodize additives absorb heat in the pore structure area to a considerable degree through endothermic reactions which absorb hot sulfuric acid reducing dissolution. This results in harder anodic coatings and faster formation/buildup rates.
- Various slow (Low Frequency Square Wave) high and low pulse systems which take advantage of the recovery effect function very well with recorded success.
- Pulse ramp systems introduce Relaxation Time, Recovery Effect, and Variable Pulse Time Rates to the process when all systems are running efficiently.
- Anodize additives and Pulse Ramp Systems reduce heat in the pore structure together through various reactions and methods. Therefore, they should be used together for maximum efficiency.
- Pulse ramp systems function together with anodize additives by providing the relaxation time and recovery effect, which allow the chemical reactions to go to completion with greater efficiency.
- When anodize additives and pulse ramp systems are both used together on the same process tank it is possible to operate at very high temperatures up to 110°F on a production basis. This has particular advantages.

    1. Better Dye Capability
    2. Finer Final Micro-finish
    3. Power Savings (KWH, Refrigeration)

- The capacitance shunt discharge system represents a very effective way to further reduce heat and voltage in the pore structure allowing anodize additives to function more efficiently at lower energy levels.
- All high tech special alloys can be processed with current efficiency producing harder coatings and practically no chance of burning when chemical additives and pulse ramp are used together in the same process tank. The following alloys are included in this high tech area.

    2011
    2219
    7050
    7178
    A-203, 206
    High Si Die Castings

- After adding the capacitance shunt discharge unit to existing pulse ramp systems (15-100 CPM), it is possible to process 2000 series alloys (2011, 2024) at current densities up to 160 ASF. Hard anodize coatings 1.5-2.0 mils thick were produced in 10-15 min at very low voltages (10-12 Volts).

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