Electrolytic Coloring of Hard Anodized Aluminum Alloys

Leonid M. Lerner, Sanford Process Corporation, Natick, MA

According to the recommendations of the Aluminum Association, the preferred aluminum alloys for two-step coloring are AA1XXX, AA3XXX, AA5XXX and AA6XXX. Results of the following study will be presented: (1) To find whether the low voltage DC+AC power supply used as the first step procedures in two-step electrolytic coloring would demonstrate better results in color acceptance and hardness on different series of aluminum alloys, especially 2XXX and 7XXX series; (2) to compare the Taber[a] abrasion resistance test between the two processes; and (3) to determine the maximum time break between first and second step in the two-step coloring process and compare between the two processes.

For more information, contact:
Leonid M. Lerner
Sanford Process Corporation
65 North Ave.
Natick, MA 01760
Phone 508-653-7860
FAX 508-653-7832
www.sanfordprocess.com

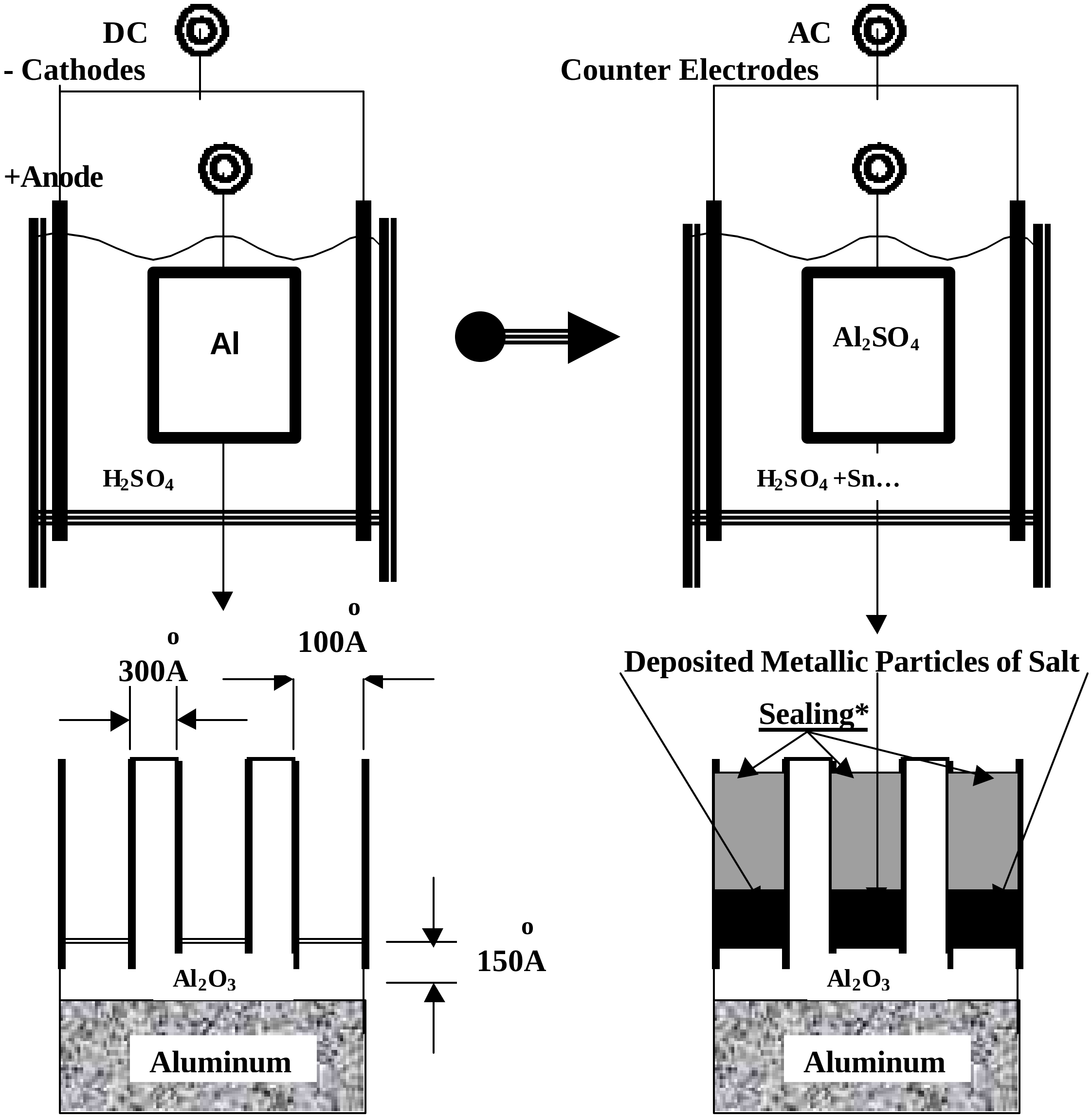
INTRODUCTION

The electrolytic coloring ("two-step") process was first in use in Europe and Asia during the 1960's (Asada Process), and was introduced in the USA during the 1970's by ALCAN. The earliest claim to coloring anodized aluminum belongs to Italian scientist Dr. V. Caboni. Dr. Caboni received an Italian patent in 1936 for impregnating aluminum oxide film with finely divided metal from aqueous solutions of the salts of copper, nickel, silver or metals electropositive to aluminum. The final product of the two-step process is conventional anodized (soft) oxide film with coloring done in a subsequent step, as shown in Fig.1. The coloring is produced by electrochemical action using a proprietary second step electrolyte, which contains the dissolved metal salts of tin, cobalt, nickel or others.

Alternate Current (AC) power is applied to the process tank by means of a counter–electrode. The applied AC power deposits metallic particles (pigment) of salt in the pores of the "first step" aluminum oxide film. The color is developed as a result of the optical effect produced by light scattering of metals, which have been deposited in the pores of oxide film. The electrolytically colored oxide film demonstrates very good weathering and corrosion resistance vs. colored oxide film formed by immersion in organic dye or in an inorganic metal salt. The differences between immersion in organic/inorganic dye and electrolytic coloring are:

1. In Immersion, the absorption of dye/salts occurs on the top portion of the pores while in two-step coloring metallic colloids deposit at the base of pores. (See Fig.2)
2. The organic dye may fade or discolor under sunlight while electrolytic coloring has excellent light resistance to fading caused by light.
3. The organic/inorganic dye will remove if the oxide film partially wears out vs. electrolytic coloring. (See Photos ##1,2 & 3).

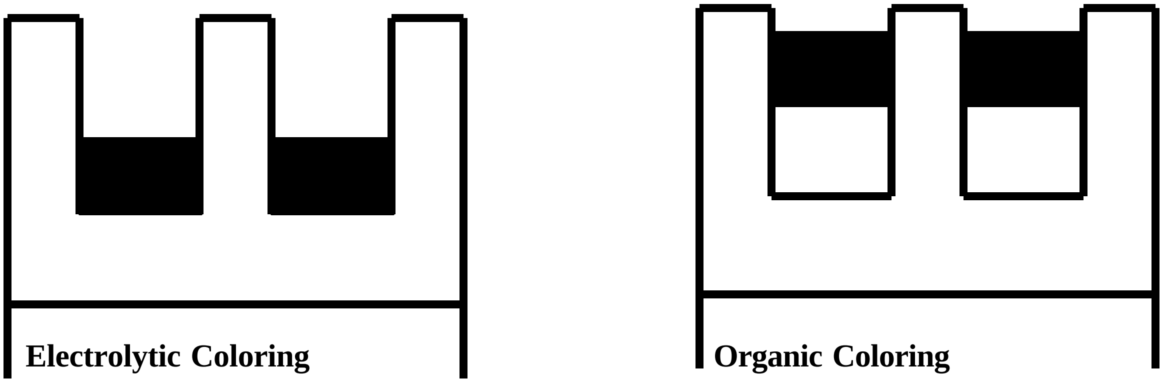
Conventional ”Two-step” Electrolytic Coloring Process



Conventional (soft) Anodizing Oxide Film

Conventional (soft) Color Anodizing Oxide Film

Fig.1



Electrolytic Coloring
***(dyeing with metal salts + AC current*)**

Organic Coloring
***(dyeing without current*)**

Fig.2

BACKGROUND OF STUDY

According to the recommendations of the Aluminum Association[1], the preferred aluminum alloys for "two-step" coloring are AA1XXX, AA3XXX, and AA5XXX & AA6XXX. The aluminum alloys of 2XXX, 7XXX series and casting are not recommended for electro coloring because of poor results.

The purpose of our study was:

1. To find whether the low voltage DC+AC Power Supply[2], used as the first step procedure in "two-step" electrolytic coloring, would demonstrate better results in color acceptance and hardness on different series of aluminum alloys, especially 2XXX and 7XXX series.
2. To compare the Taber™ abrasion resistance test between the two processes.
3. To determine the maximum time break between first and second step in the "two-step" coloring process and compare between the two processes.

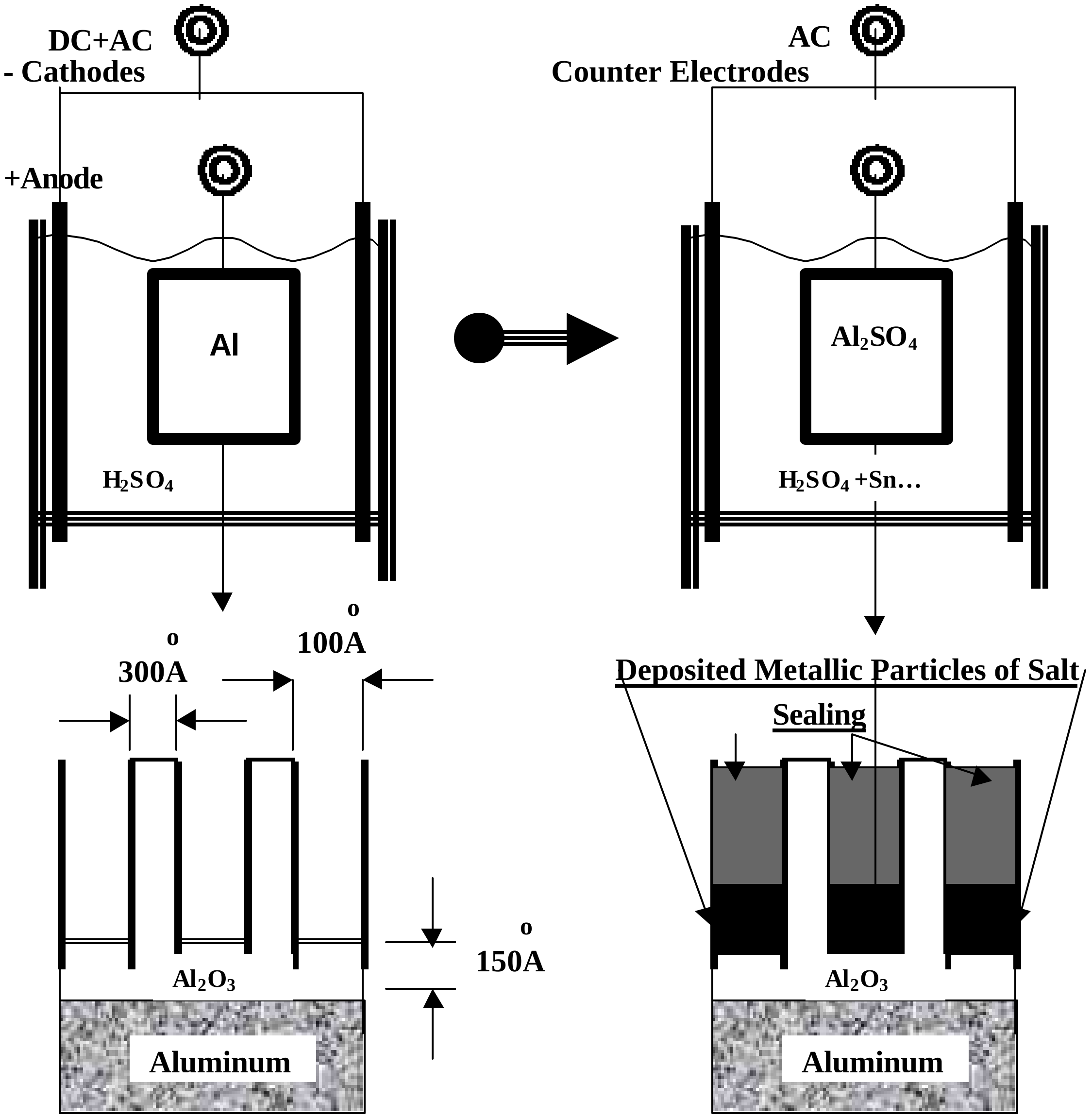
In our studies we employed 2 different power supplies. For conventional anodizing as first step we used a DC Power Supply (0-15 VDC) and a DC+AC Power Supply[2] (0-12VDC). (See Fig.1 & Fig.3) All samples were 4"x 4" squares (32 sq. in) of 2024-T3, 6061-T6 & 7075-T6 aluminum alloys. Prior to this study some "first step" anodized samples, including 2024-T6, were sent to Clariant laboratory for electrolytic coloring. The time break between the "first step" (DC+AC anodizing) and "second step" (electrolytic coloring) was approximately 72 hours. <u>All samples</u> show a good color acceptance. (See Tables 4 & Photos ##6,7, & 9)

The electrolytic coloring as "second step" was done using an AC power supply (60 Hz) with a maximum constant voltage of 20VAC. The counter–electrode in the plastic process tank was made from stainless steel. The bus bar was made from aluminum 6061-T6. A filtration pump in conjunction with a 10-micron filter was installed. A pre-mix electrolyte[*] was used. In most cases the coloring cycle was 10 minutes. All samples were sealed for 5 minutes in (185ºF) Nickel Acetate solution.

---

[*] Sandocolor™, Clariant Corporation, Charlotte, NC

DC+AC ”Two-step” Electrolytic Hard Coloring Process



Quantum™ Hard Anodizing Oxide Film

Electrolytic (hard) Color Oxide Film

Fig.3

TABLES

Table 1 displays the different data related to the first step anodizing with the same electrolytic coloring techniques for all samples in the experiment.

Column#1	is the name of the process and identifies the part number of each sample. The power supplies used were a conventional DC Voltage and a proprietary Low Voltage DC + AC_2.
Column#2	contains the electrolyte composition.
Column#3	contains the electrolyte concentration in grams per liter.
Column#4	contains the temperature of electrolyte in C° during the process.
Column#5	contains the temperature of electrolyte in F° during the process.
Column#6	shows the time of the hard coating process in Minutes.
Column#7	shows the maximum voltage used in the process.
Column#8	shows the maximum current density (Amps/sq. ft.) reached during the process.
Column#9	shows the thickness of the coating in mils, determined by averaging at least nine measurements from different spots on the samples.
Column#10	contains the type of aluminum alloy.

TABLE 1

Process, Conditions & Comparative Data for First Step Anodizing Processes
(with the same electrolytic coloring techniques for all samples)

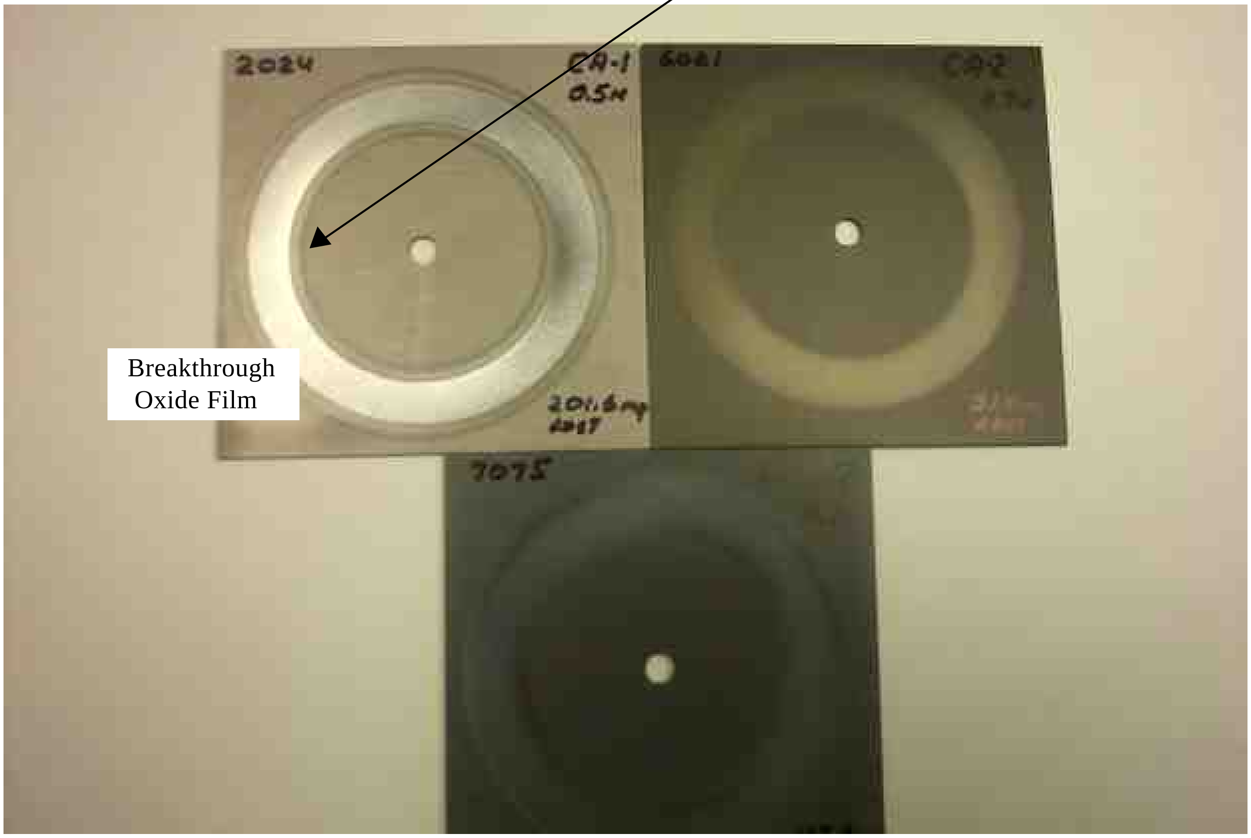
Process Name & Sample ##	**Process Tank Electrol.**	**Electrol. Concentr. (gr/l)**	**Temp. C°/F°**		**Process Time (min)**	**Volt. (max) V**	**Current Density (A/sq.ft)**	**Film Thick (mils)**	**Al. Alloy**
1	2	3	4	5	6	7	8	9	10
Conventional DC anodizing									
CA-1	Sulfuric acid	180	21	70	50	16	15	0.5	2024-T3
CA-2								0.9	6061-T6
CA-3								0.9	7075-T6
CA-1A*								0.5	2024-T3
CA-2A*								0.9	6061-T6
CA-3A*								0.9	7075-T6
DC+AC Hard Anodizing									
2S#4									
2S#6	Sulfuric acid with organic additive	200	21	70	15	12.3	67.5	1.1	6061-T6
2S#7		-/-	-/-	-/-	15	14.6	75.0**	1.2	2024-T3
2S#8		-/-	-/-	-/-	15	14.6	75.0**	0.7	6061-T6
2S#9		-/-	-/-	-/-	15	14.6	75.0**	2.4	7075-T6
2S#10		-/-	-/-	-/-	5	13.9	135.0	0.8	6061-T6
2S#11		-/-	10	50	6	18.0	135.0	0.9	6061-T6
2S#12*		300	-/-	-/-				0.5	6061-T6
2S#13*		200	-/-	-/-	9	12.6	90.0**	0.3	2024-T3
2S#14*		-/-	-/-	-/-	9	12.6	90.0**	0.5	6061-T6
2S#12A		-/-	-/-	-/-	9	12.6	90.0**	1.0	7075-T6
2S#14A		-/	-/	-/	15	12.0	31.0	1.0	2024-T3
		-/	-/	-/	15	11.5	32.0	0.5	7075-T6

**-The electrolytic coloring was done after 72 hours*
*** - Simultaneous run*

TABLE 2
TABER TEST

For DC Anodizing Process + Electrolytic Coloring
(Sulfuric acid 180 gr/l. Electrolyte temperature 70ºF)

Alloy & part #		Thickness (mil)	Weight		Weight Loss (g)	Wear Index
			Before	After		
2024-T3	**CA-1**	**0.5**	**45.1316**	**44.9300**	**0.2016**	**20.16**
6061-T6	**CA-2**	**0.9**	**42.7254**	**42.6940**	**0.0314**	**3.14**
7075-T6	**CA-3**	**0.9**	**44.9770**	**44.9297**	**0.0473**	**4.73**



Breakthrough
Oxide Film

Photo #10

TABLE 3
TABER TEST

Low Voltage DC+AC Hardcoating Process+ Electrolytic Coloring
(Sulfuric acid with organic additive 200/300 gr/l. Electrolyte temperature 70ºF)

Alloy & Part #	Thickness (mil)	Weight		Weight Loss (g)	Wear Index
		Before	After		
6061-T6 2S#4	1.1	45.6508	45.6238	0.0027	2.70
2024-T3 2S#6	1.2	42.8019	42.7327	0.0692	6.92
6061-T6 2S#7	0.7	42.3311	42.3111	0.02	2.00
7075-T6 2S#8	2.4	45.1356	45.0838	0.0518	5.18
6061-T6 2S#9	0.8	43.5292	43.5058	0.0234	2.34
6061-T6 2S#10	0.9	43.4975	43.4752	0.0223	2.23
6061-T6 2S#11	0.5	42.8086	42.7816	0.027	2.70
2024-T3 2S#12A	0.5	42.4076	42.3624	0.0452	4.52
7075-T6 2S#14A	1.0	45.6549	45.6249	0.030	3.00

Relative Humidity (aver.) – 50; Temperature (aver.) – 75ºF

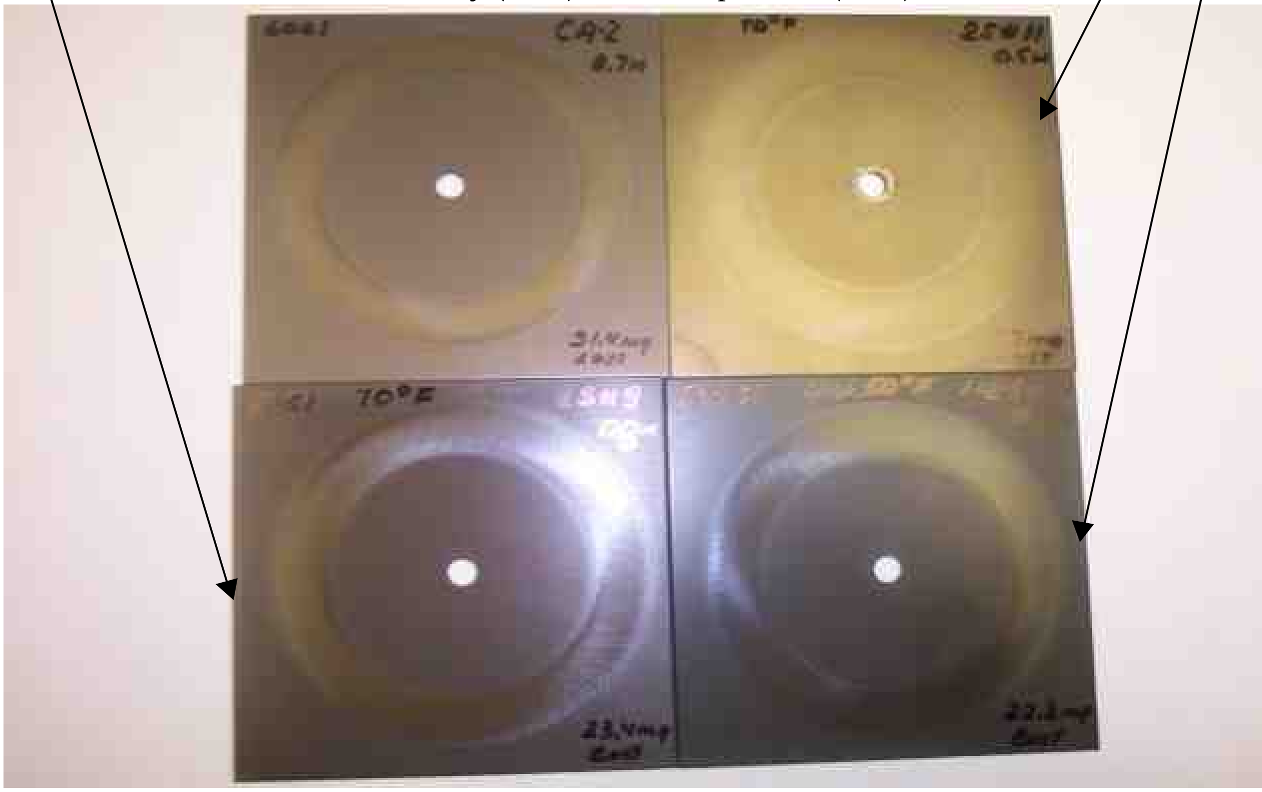


Photo #11

RESULTS AND ANALYSIS

Electrolytic Dyeability

Our study of samples in Photo # 11 shows:

Different intensity of dark color on 6061-T6 electrolytic colored aluminum alloys between Conventional DC anodizing sample (CA-2) and DC+AC hard anodizing sample (2S#9)

The DC+AC process visually demonstrates deep dark and uniform appearance of color.

Time Break Between First and Second step in "two-step" Electrolytic Coloring Processes

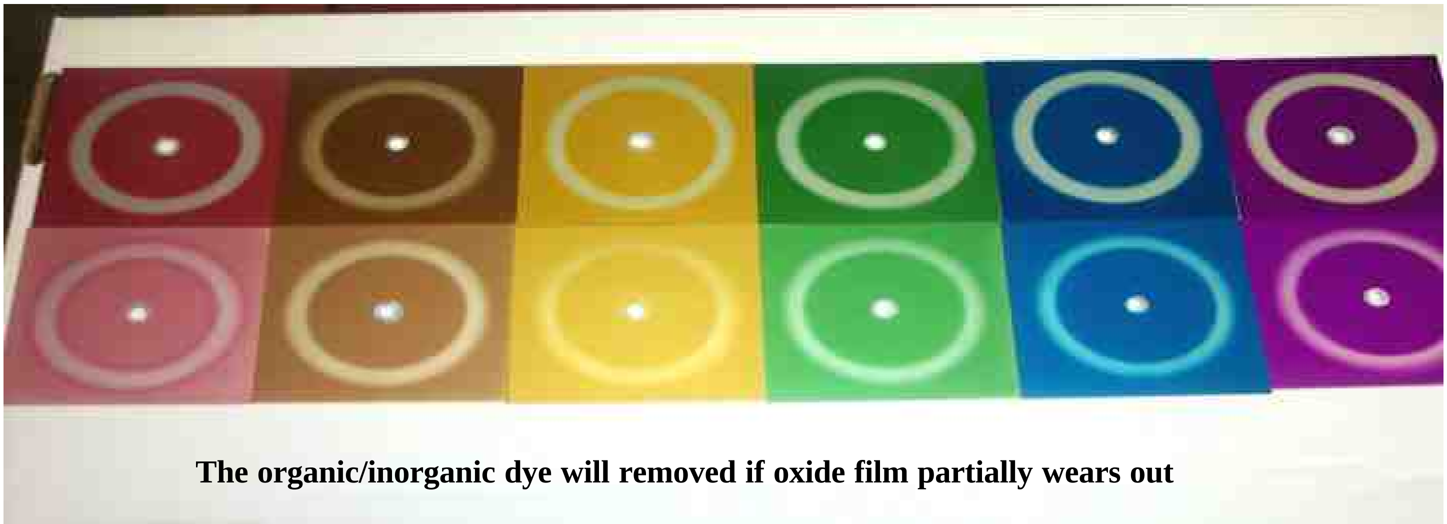
72 hours after the different anodizing processes (DC and DC+AC), the samples (2024-T3, 6061-T6 & 7075-T6 aluminum alloy) were electrolytically colored during 10 minutes. The samples run by DC+AC process demonstrate very promising results on absorption and uniformity of color after spending long hours in the open air as compared to the conventional DC process, which showed the different intensity, uniformity and poor dyeability. (See Photos #4 & 5).

Taber Abrasion Tests

Mil-A-8625F specifies that the anodic coating shall have a maximum wear index of 3.5 mg/1000 cycles (or 35 milligrams of weight loss per 10 thousand cycles on aluminum alloys having a copper content of 2 percent or higher) and 1.5 mg/1000 cycles (or 15 milligrams of weight loss per 10 thousand cycles on other aluminum alloys). We cannot compare the abrasion resistance of oxide films after electrolytic coloring to Military Specification numbers, but we try to compare results between the two processes (DC & DC+AC).

Our study of Tables 2 & 3 shows:

The abrasion results produced on 2024-T3, 6061-T6 & 7075-T6 aluminum alloys after the DC+AC "first step" process surpassed the results of the Conventional Anodizing DC process. The Wear Index results of coatings produced in DC+AC anodizing process exceed coatings produced by Conventional DC process.



The organic/inorganic dye will removed if oxide film partially wears out

Photo #1

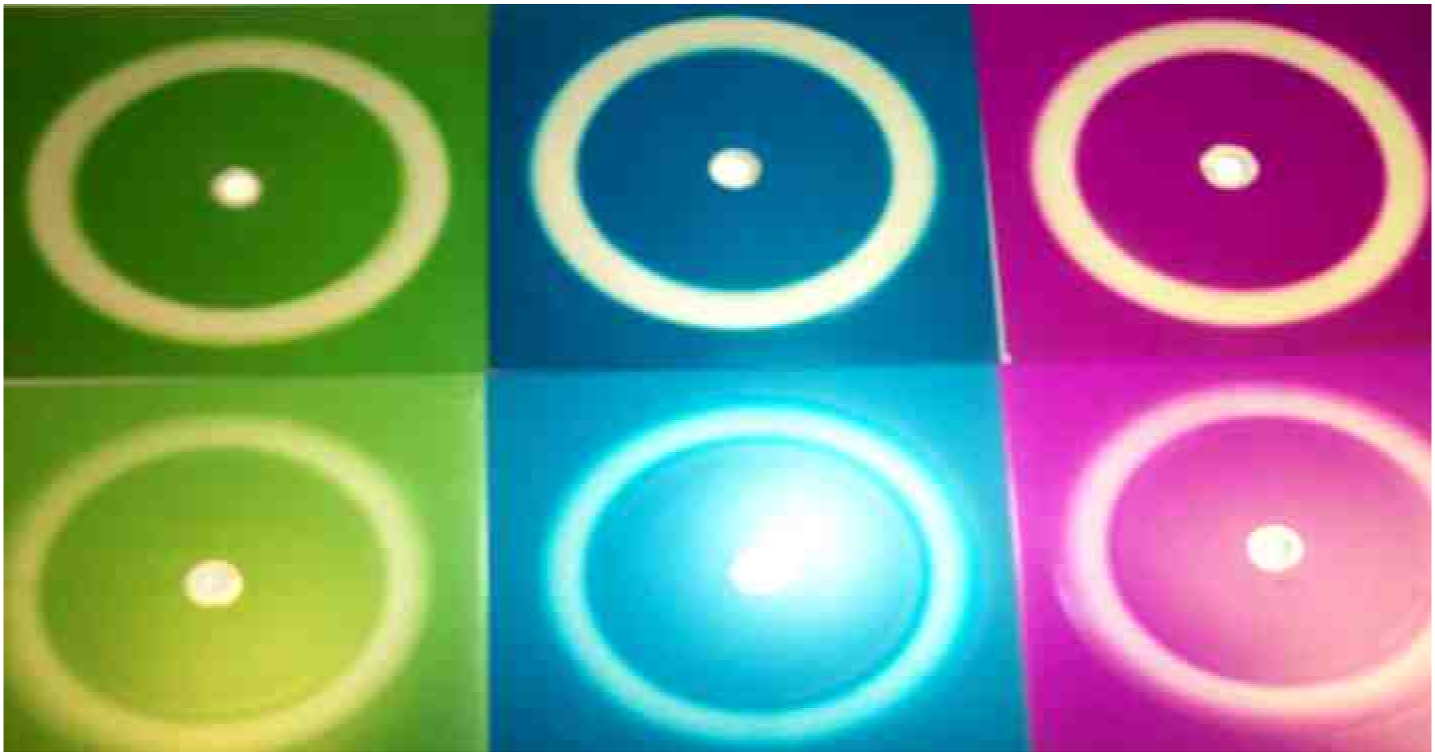
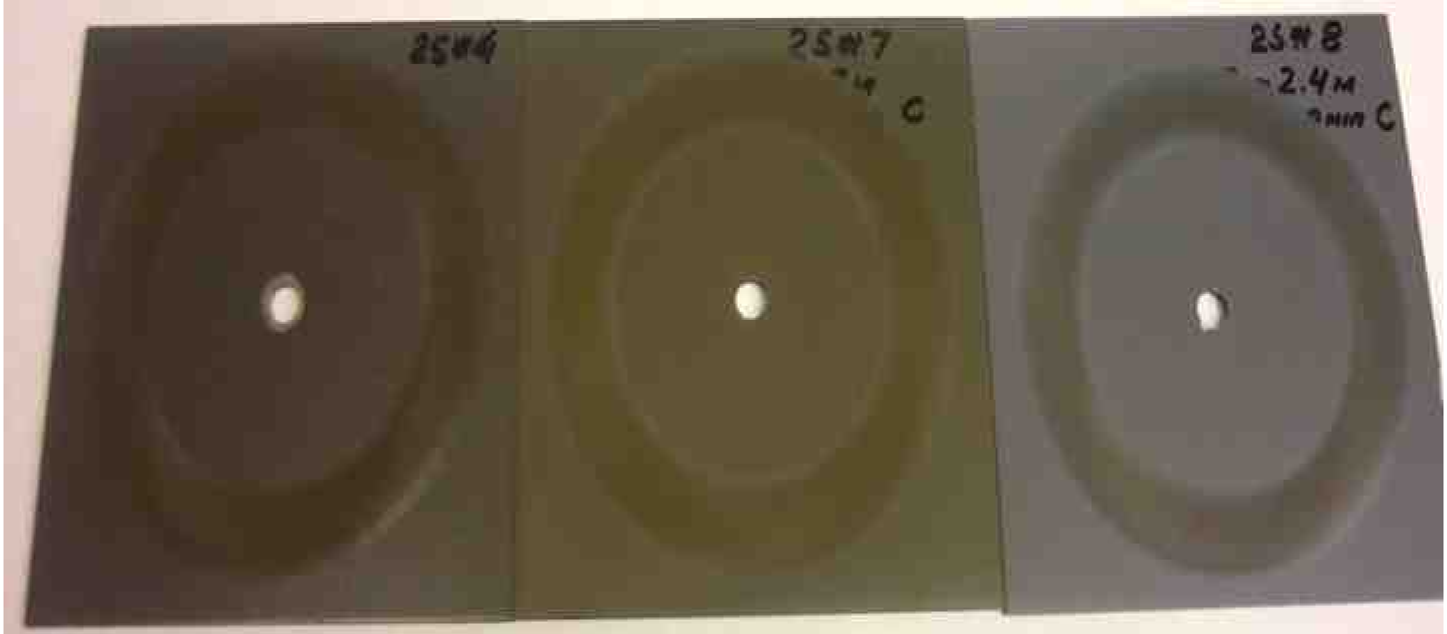
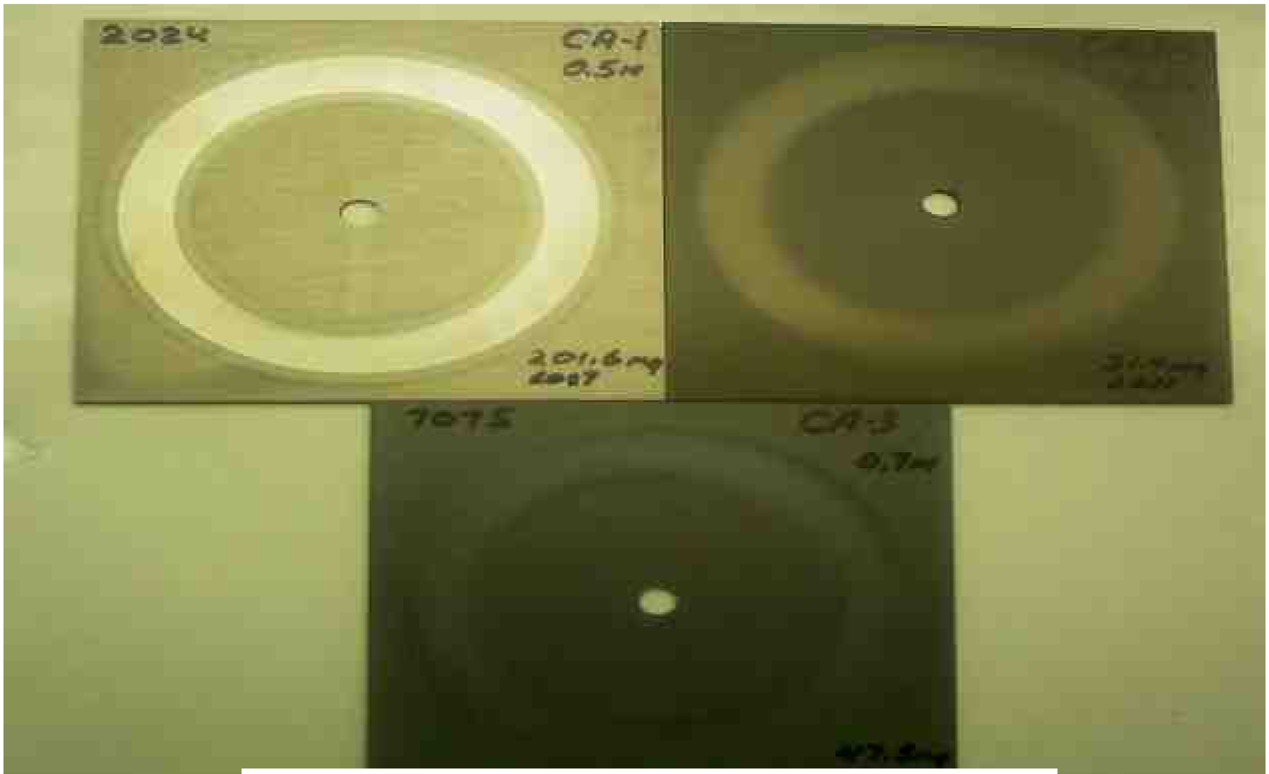


Photo #2



Color appearance on 2024-T3, 6061-T6 & 7075-T6 after DC+AC ”Two-step” Electrolytic Hard Coloring Process

Photo # 3

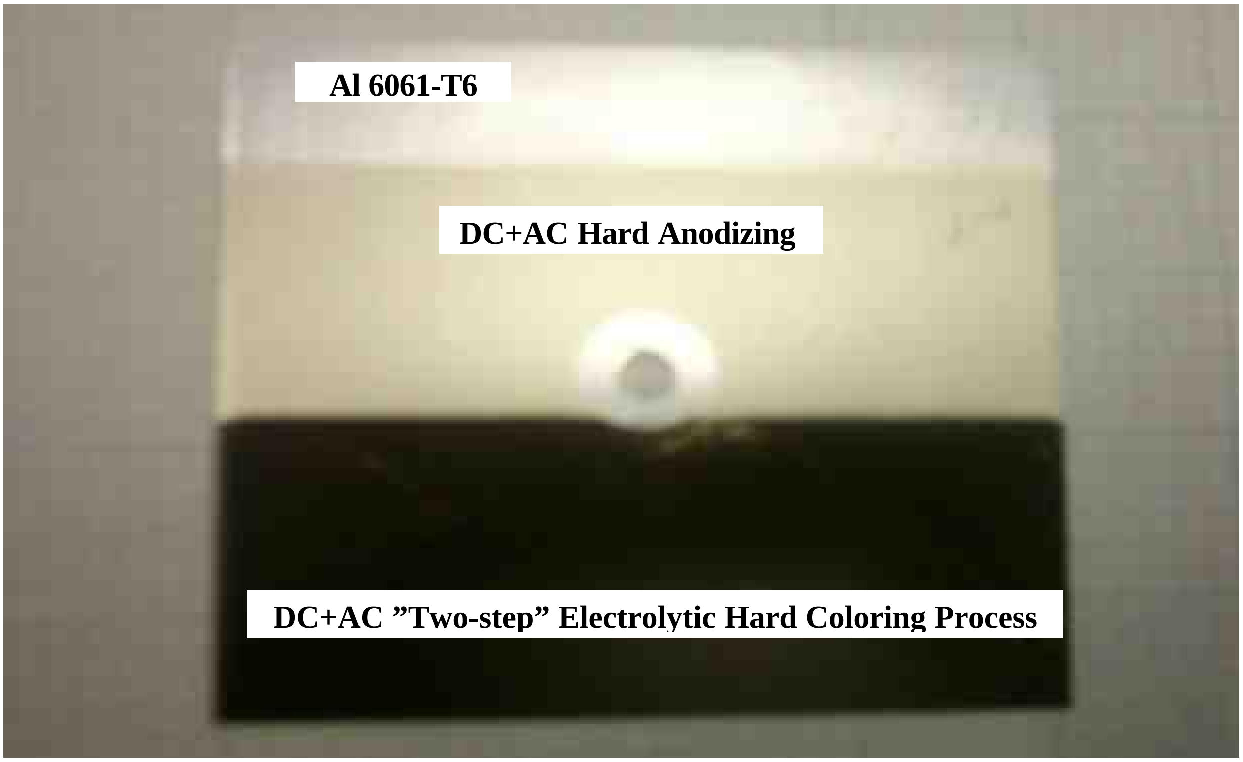


Conventional Anodizing + ”Two-step” Coloring Process

Photo # 4

DC+AC ”Two-step” Electrolytic Hard Coloring Process

Photo # 5



Photos # 6

Photos # 7

6061-T6511 aluminum alloy with 0.2-0.3 mils of hard coating by DC+AC process (70ºF) and electrolytic coloring

Photo #8

<u>All samples</u> shows good color acceptance like as would be for standard Type II process

Photo #9

Acknowledgments:
I would like to thank my colleagues in Sanford Process Corporation (Andrew Corcoran) and Duralectra Inc. (Raquel Lakari & Bob Burns) for their support and assistance during experiments reported here.

Bibliography: **1993 PF Directory “Anodizing Aluminum” by J.G. Hecker, Jr.**
1972 Surface “Treatment and Finishing of Aluminum” by S.Wernick & R.Pinner